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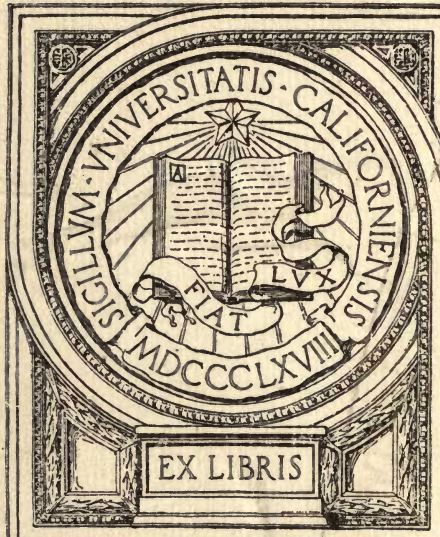

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CHEMICAL THEORY FOR BEGINNERS

ATOMIC WEIGHTS OF THE ELEMENTS.

Name.	Symbol.	Approximate Value.	Accurate Value. Oxygen = 16.	Name.	Symbol.	Approximate Value.	Accurate Value. Oxygen = 16.
Aluminium	Al	27	27·08	Molybdenum	Mo	96	96·1
Antimony	Sb	120	120·3	Nickel	Ni	59	58·5
Arsenic	As	75	75·00	Niobium	Nb	94	94·2
Barium	Ba	137	137·04	Nitrogen	N	14	14·041
Beryllium	Be	9	9·05	Osmium	Os	191	191·0
Bismuth	Bi	209	208·9	Oxygen	O	16	16·000
Boron	B	11	11·0	Palladium	Pd	106·5	106·7
Bromine	Br	80	79·963	Phosphorus	P	31	31·03
Cadmium	Cd	112	111·9	Platinum	Pt	195	195·0
Cæsium	Cs	133	132·88	Potassium	K	39	39·136
Calcium	Ca	40	40	Rhodium	Rh	103	103·1
Carbon	C	12	12·003	Rubidium	Rb	85	85·44
Cerium	Ce	140	140·2	Ruthenium	Ru	102	101·7
Chlorine	Cl	35·5	35·453	Samarium	Sm	150	150
Chromium	Cr	52	52·07	Scandium	Sc	44	44·09
Cobalt	Co	59	59·1	Selenium	Se	79	79·07
Copper	Cu	63·5	63·60	Silicon	Si	28·5	28·4
Didymium	Di	142	?	Silver	Ag	108	107·938
Erbium	Er	166	166	Sodium	Na	23	23·058
Fluorine	F	19	19·05	Strontium	Sr	87·5	87·52
Gallium	Ga	70	69·9	Sulphur	S	32	32·063
Germanium	Ge	72	72·32	Tantalum	Ta	183	182·8
Gold	Au	197	197·3	Tellurium	Te	125	125
Hydrogen	H	1	1·008	Thallium	Tl	204	204·15
Indium	In	114	113·7	Thorium	Th	232	232·4
Iodine	I	127	126·864	Tin	Sn	118	118·10
Iridium	Ir	193	193·4	Titanium	Ti	48	48·13
Iron	Fe	56	56·0	Tungsten	W	184	184
Lanthanum	La	138	138·5	Uranium	U	239	239·4
Lead	Pb	207	206·91	Vanadium	V	51	51·21
Lithium	Li	7	7·030	Ytterbium	Yb	173	173·2
Magnesium	Mg	24	24·35	Yttrium	Y	89	89·0
Manganese	Mn	55	55·09	Zinc	Zn	65	65·38
Mercury	Hg	200	200·4	Zirconium	Zr	90·5	90·67

CHEMICAL THEORY

FOR BEGINNERS

BY

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AND

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PREFACE

OUR object in writing this little book has been to assist beginners in obtaining an elementary knowledge of the principles upon which modern chemistry is based. The smaller text-books which deal with Systematic Chemistry usually treat theoretical matters so lightly that the student seldom obtains any satisfactory grasp of these during the earlier portion of his studies; while in the larger treatises the same subjects not infrequently receive similar scant attention, because the student is supposed to have been introduced to them already. For example, beginners are seldom made to understand the full significance of chemical formulæ, although they are usually taught to use them at a very early stage in their studies. These chemical formulæ are the outcome and embodiment of many facts and theories, and their logical introduction into a course of chemistry can only take place at a comparatively late period. Their convenience, however, is felt to be so great, that the student is usually brought face to face with them prematurely, at a time when he can neither understand their origin nor appreciate their import; and later, when he begins his more advanced studies, he is often assumed to be quite conversant with them.

In the first part of the book we have endeavoured to remedy this defect, by setting forth in a simple and connected manner, the nature of the facts (and of the theories derived from them) with which the chemist must be acquainted before he is justified in employing chemical formulæ at all.

The later chapters contain, amongst other things, an entirely non-mathematical exposition of the more important principles of General Chemistry, which has made such great progress of late years, especially in the departments of solution and electrolysis. Although the new theories in this branch of the subject are still received with reserve by many British chemists, we have not hesitated to place them before the beginner, convinced as we are of their usefulness, and of their eventual general recognition.

Many of the subjects dealt with have been intentionally, and indeed necessarily, very shortly treated. We hope, however, that enough has been said respecting the most important matters to make the book serve as an easy and yet sufficient introduction to the larger text books, both of Systematic and of General Chemistry.

L. D.
J. W.

EDINBURGH, *June* 1892.

CONTENTS

CHAPTER		PAGE
	INTRODUCTION.—ON UNITS AND MEASUREMENT .	1
1.	SOLIDS—LIQUIDS—GASES	5
2.	ELEMENTS AND COMPOUNDS	11
3.	CHEMICAL ACTION—GENERAL CONDITIONS . .	16
4.	CHEMICAL ACTION—CHARACTERISTICS . . .	26
5.	LAWS OF CHEMICAL COMBINATION . . .	39
6.	ILLUSTRATIONS OF CHEMICAL ACTION—COMBUSTION	50
7.	ILLUSTRATIONS OF CHEMICAL ACTION—OXIDATION AND REDUCTION	60
8.	LAWS OF BOYLE AND OF CHARLES . . .	72
9.	DENSITY—VAPOUR DENSITY	81
10.	AVOGADRO'S LAW	88
11.	DETERMINATION OF ATOMIC WEIGHTS . . .	94
12.	CHEMICAL NOTATION—SYMBOLS, FORMULÆ, AND EQUATIONS	107

CHAPTER PAGE

13. Bases—Acids—Salts 121

14. The Kinetic Molecular Theory . . . 139

15. Mass Action and Dissociation 147

16. Solutions 160

17. Electrolysis 176

18. Equivalence 187

19. Substitution and Double Decomposition . 198

20. Chemical Constitution 208

21. The Periodic Law 221

Index 237

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INTRODUCTION

ON UNITS AND MEASUREMENT

WHEN we measure anything—be it a length, a weight, a time, or any other magnitude—we express the result of our measurement by means of a number and of a name. Thus we speak of a length of 5 feet, and of a weight of 20 pounds. The name expresses the unit or standard with which we compare the quantity to be measured, and the number tells us the number of times the quantity contains this unit.

In the above instances we have adopted as unit of length the foot, and as unit of weight the pound. It evidently depends upon the choice of the unit what the number to express a certain quantity will be. 5 feet and 60 inches both stand for the same length, the unit in the second case, however, being twelve times smaller than in the first, so that it requires twelve times as many of these small units to make up the given length as it does of the larger units.

The units employed to measure length, weight, etc., in everyday life differ in different countries, but scientific men of every nationality have practically all agreed to adopt one system of units, for the sake of uniformity, and the possibility of easy comparison of the results of different observers. The system of weights and measures chosen is the French or Metric System.

The unit of length in this system for scientific purposes is the *centimetre*, which is equal to ·3937 inches. There are often used, besides the centimetre, decimal multiples or submultiples of it, when the length expressed in centimetres would give numbers either inconveniently large or inconveniently small. The relations of these to the centimetre are given in the following table—

1 centimetre (cm.) = 10 millimetres (mm.)
100 centimetres = 1 metre (m.)
1000 metres = 1 kilometre.

The unit of surface is a square measuring 1 centimetre each way, and is called the square centimetre (sq. cm.). It is equal to ·155 square inches.

For unit of volume we take a cube, each of whose edges measures a centimetre in length. This unit is called the cubic centimetre (c.c.).

1000 c.c. = 1 litre (l.) = 1·76 pints.

The unit of mass—quantity of matter—is the mass of 1 c.c. of pure water at the temperature at which water occupies the smallest volume, viz. 4° Centigrade (see p. 82). This unit is called the *gram*. Its multiples and submultiples are—

1 kilogram (kilo.) = 1000 grams (g.)
1 gram = 10 decigrams (dg.)
= 100 centigrams (cg.)
= 1000 milligrams (mg.)
1 gram = 15·432 grains. 1 kilo = 2·2046 pounds.

Since the mass of 1 c.c. of water at 4° is 1 gram, the mass of 1 litre, or 1000 c.c., of water at the same temperature is 1000 grams, or 1 kilogram. These masses are also all known, under the same names, as *weights*; we ordinarily talk of a substance being so many grams weight instead of grams mass. Strictly speaking, the

weights of these masses are the forces by which they are attracted downwards to the earth, and which vary very slightly as the masses are moved from place to place. But as at any one place weights are proportional to masses, and the method of weighing by means of a balance therefore compares masses as well as weights, we may for almost all purposes use the word weight instead of mass without being led into error.

The scale in which temperature is measured is the Centigrade or Celsius scale. On it the freezing-point of water is 0° and the boiling-point of water at the normal atmospheric pressure 100°. On the Fahrenheit scale, which is in ordinary use in this country, the freezing-point of water is 32°, and the boiling-point 212°. The range between these two fixed points is divided into 100° in the Centigrade scale and 180° in the Fahrenheit scale. The Centigrade degree is thus equal to 1·8 Fahrenheit degree. A convenient rule for converting temperatures Centigrade into temperatures Fahrenheit is the following: Double the number of degrees Centigrade, subtract a tenth of the number thus obtained, and add 32. Suppose the temperature Centigrade is 50°; then we have—

$$\begin{array}{r} 50\times 2 = 100 \\ -\ 10 \\ \hline 90 \\ 32 \\ \hline \end{array}$$

122° Fahrenheit.

If the temperature Centigrade is − 50°, we get—

$$\begin{array}{r} -50\times 2 = -100 \\ -(-10) = +\ 10 \\ \hline -90 \\ +32 \\ \hline \end{array}$$

− 58° Fahrenheit.

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In what follows we shall always use the Centigrade scale in measuring temperature, unless the contrary is distinctly specified.

The beginner must be reminded that heat is a very different thing from temperature, and is measured in another unit. A litre of boiling water has the same temperature as two litres of boiling water, but only half as much heat. The unit of heat usually employed is that quantity which raises the temperature of 1 g. of water 1 degree at the ordinary atmospheric temperature (15° to 18°). The number of these units required to raise the temperature of 1 g. of a substance 1 degree starting from a certain temperature is called the specific heat (more properly the thermal capacity) of that substance at that temperature.

CHAPTER I

SOLIDS—LIQUIDS—GASES

ALL material substances which are met with in nature may be divided into classes, according to what is called their **state of physical aggregation.** Three such classes may be conveniently distinguished, which embrace substances in the **solid** state, in the **liquid** state, and in the **gaseous** state. Examples of substances illustrating these three states on a very large scale are furnished respectively by the rock masses of the earth's crust, by the water of the ocean, and by the earth's atmosphere.

Many instances are known of substances which are capable of existing, under different conditions, in all three of these states. Thus, for example, the substance which in the liquid state we call water can be converted, by cooling, into the solid state as ice, and, by heating, into the gaseous state as steam.

Water freezes at 0° and boils at 100°.

Note that the white cloud which is commonly called "steam" really consists of minute drops of *liquid* water. True steam or vapour of water is colourless, transparent, and invisible, like the gases of the atmosphere.

Experiment 1.—Boil some water in a test-tube. Observe when the water is boiling briskly that the steam which is present in the upper portion of the tube is in-

visible, and that the familiar white cloud is only visible at the mouth of the tube, where the steam becomes condensed to liquid particles by contact with the cooler surrounding air.

Alcohol, which is a liquid at ordinary temperatures, is converted into vapour at 78·3°. It solidifies when cooled to the extremely low temperature of − 130°.

Sulphur and iodine, which are solid substances at ordinary temperatures, are also known in all three states. Sulphur melts when moderately heated and forms a limpid, pale brown liquid; and this liquid boils at a high temperature, yielding gaseous sulphur as a dark, reddish brown vapour. Vapour of sulphur, like vapour of water, is transparent, but, unlike vapour of water, it is coloured, and is therefore visible.

Sulphur melts at 111° and boils at 440°.

Experiment 2.—Place a few crystals of iodine in a test-tube and heat gently over the flame of a Bunsen burner. Observe that at a comparatively low temperature the iodine melts, forming a very dark, nearly black liquid; and that, on further heating, this liquid boils, forming a deep violet-coloured vapour. Observe also that the vapour, on cooling again, condenses to form small crystals of iodine on the interior of the test-tube.

Iodine melts at 113° and boils at 200°.

Note particularly that when ice melts and when steam condenses, liquid water is formed again. Note also that in the cases of sulphur and of iodine the solid substances are formed again when the vapours and the liquids are sufficiently cooled.

There are many substances which are only known in one or in two of the foregoing states. Quicklime, for instance, is only known in the solid state, and does not melt at the highest attainable temperature. Sugar, again, is a solid at ordinary temperatures. It can be

liquefied by careful heating; but it cannot be obtained as a gas, because at a temperature not much above the melting-point the liquid undergoes a kind of change, which results in the production of various new substances, including gases, which are no longer sugar, and do not condense again on cooling to form the original solid.

Experiment 3.—Carefully heat a small quantity of cane sugar in a test-tube, eventually heating strongly. Observe that on moderately heating the sugar, it melts to form an almost colourless liquid; that on heating this liquid somewhat more strongly it gradually darkens in colour, while bubbles of gas are given off; that the gas so given off possesses a peculiar pungent smell, carries with it a quantity of white smoke, and can be lighted at the mouth of the tube, where it burns with a bluish, feebly luminous flame; that drops of liquid condense on the cool upper part of the tube; and that the substance which remains in the test-tube is black and highly porous, and does not resemble sugar in its appearance or properties.

Cane sugar melts at 160° and above 190° the liquid darkens rapidly.

Note particularly the essential difference in the action of heat on melted iodine and on melted sugar in Experiments 2 and 3 respectively. In the case of iodine the change produced is a **physical** one, the vapour formed consisting of the same substance as the liquid, only in a different state. In the case of sugar the change produced is a **chemical** one, new gaseous substances being given off and a new black solid substance remaining behind, all of which are quite different from the original sugar.

Experiment 4.—Take some *clean* pieces of lead and heat them in an iron spoon or ladle over a Bunsen burner or a fire until they melt. Observe that a gray scum forms on the surface of the melted lead, and that

on pouring out the melted metal its surface is clear and bright, while the scum remains behind in the iron vessel. The liquid metal soon solidifies. The melting of the metal and its resolidification are physical changes. The formation of the scum is a chemical change, in which a new substance is produced by the action of the oxygen of the atmosphere on a portion of the melted lead.

Many solid substances become slowly converted into the gaseous state at ordinary temperatures, without passing through the liquid state. This is the case, for example, with camphor and with iodine. The odours of camphor and of iodine may be perceived in the neighbourhood of the solid substances on account of this property, and if the substances are exposed to the air for a sufficient length of time they eventually become completely converted into vapour and disappear. Ice also slowly gives off water vapour even when its temperature is maintained below the melting-point (compare p. 146).

Many substances are known which are gases under the ordinary atmospheric conditions of temperature and of pressure. By appropriate means these can be converted into liquids, and some at least of the liquids can be converted into solids. The method of liquefying a gas may consist (1) in simply cooling it; or (2) in subjecting it to an increase of pressure; or (3), as is usually the case, in combining both of the former methods (1 and 2). In the case of every gas there is a limit of temperature below which the gas must be cooled before it can be liquefied by subjecting it to any pressure, however great. This limit of temperature is called the *critical temperature*, or critical point. The critical temperatures of different gases lie, in many cases, widely apart.

The pungent smelling gas which is produced when sulphur burns in air (sulphurous anhydride) can be liquefied by passing it through a tube kept cold by immersion in a mixture, in the proper proportions, of snow and

salt. The liquefied substance freezes when it is further sufficiently cooled.

Liquid sulphurous anhydride boils at $-8°$, and freezes when cooled below $-76°$.

By mixing together 2 parts by weight of snow or pounded ice, and 1 part by weight of salt, a mixture having the temperature of $-17{\cdot}8°$ can be obtained.

Oxygen, one of the gases contained in the atmosphere, can only be obtained in the liquid state by the combined influences of an exceedingly low temperature and of a high pressure.

Oxygen is condensed to the liquid state at $-118°$ by a pressure equal to fifty times the average pressure of the atmosphere at the sea level.

The critical temperature of sulphurous anhydride is 155°.

When any solid substance is liquefied, and when any liquid is converted into gas, without undergoing a chemical change, heat is absorbed by the substance which undergoes this physical change, but its temperature does not rise. Suppose, for example, heat to be applied to a piece of ice, the temperature of which is 0°, the ice is not warmed, *but some of it is melted* and converted into water at 0°; or suppose heat to be applied to water at 100°, the water is not further heated, but some of it is converted into water vapour at 100°. To this heat, which must be supplied to substances in order that they may be changed from solid to liquid and from liquid to gas, but which does not cause any rise in their temperature, the name **latent heat** was given by Black, who first observed in 1762 the phenomena concerned. This latent heat is given out again when the physical change takes place in the reverse direction, from gas to liquid and from liquid to solid.

Solid substances may be divided into two classes according to whether they possess a **crystalline** character or not. Many substances **crystallise**, or assume

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definite geometrical forms which are called **crystals**, when they pass from the liquid or the gaseous state into the solid state, or when they separate out in the solid state from liquids in which they have been dissolved. The fragments in which common salt, sugar, saltpetre, etc. are commonly seen, are crystals or portions of crystals, and these substances are said to be crystalline. Wood, glass, leather, gelatine, etc., are non-crystalline or **amorphous** solids.

The most important lessons of this chapter for the beginner in chemistry are, that mere change of temperature of a substance or of its state from solid to liquid, from liquid to gas, from gas to liquid, or from liquid to solid, is not chemical but physical change; and that a chemical change requires the production of at least one new substance, possessing its own characteristic properties, from the original substance or substances to which that change occurs.

CHAPTER II

ELEMENTS AND COMPOUNDS

WHEN we examine the various substances which surround us in nature, or those which we can, by any method of treatment, produce from naturally occurring substances, we find that in many instances it is possible by appropriate means to break these up into two or more new substances, each entirely different in its properties from the original substance. This is, as explained in the previous chapter, a chemical change, and it is an illustration of that particular kind of change which is called **decomposition.** When, for example, mercuric oxide or the red oxide of lead (red lead) is heated, decomposition takes place, and in either case two new substances are produced.

Experiment 5.—Heat some mercuric oxide (red oxide of mercury) in a narrow hard-glass tube. Observe that the colour of the oxide changes on heating, becoming almost black; that oxygen is given off, and may be recognised by introducing into the upper part of the tube a glowing match or strip of cedar wood, which immediately bursts into flame; and that small drops of metallic mercury condense on the cooler portions of the interior of the tube. In this experiment the mercuric oxide is decomposed into mercury and oxygen. If the experiment is not continued until the whole of the oxide is thus decomposed, observe that the undecom-

posed portion again assumes its original red colour on cooling.

Experiment 6.—Perform an experiment similar to Experiment 5, only employing red oxide of lead instead of mercuric oxide. Observe that in this case also the colour of the oxide darkens at first; that oxygen is given off, which may be recognised as in Experiment 5; and that a yellowish solid substance remains in the tube at the end of the experiment. This substance is called litharge.

The new substances obtained in Experiments 5 and 6 by the action of heat on mercuric oxide and on red oxide of lead are oxygen and mercury, and oxygen and litharge respectively. It is not possible by any known method to further decompose either oxygen or mercury into two or more simpler substances, or to produce either of them by causing two or more simpler substances to combine. Litharge, on the other hand, although it cannot be further decomposed by heat alone, can be shown by other processes of *analysis* (decomposition, see p. 14) to consist of lead and oxygen. Further, it can be produced by causing lead and oxygen to combine under suitable conditions. The formation of a new substance in this way from simpler materials is called *synthesis*. Lead, like oxygen and mercury, cannot be further decomposed, nor can it be produced by synthesis.

Substances which, like oxygen, mercury, and lead, cannot be shown by methods either of analysis or of synthesis to consist of two or more simpler substances are called **elements**. Substances, on the other hand, which, like mercuric oxide, red oxide of lead, and litharge, can be proved (whether it be by a method of analysis or of synthesis) to consist of at least two simpler substances chemically combined together, are called **compounds**. The name element is thus applied to any substance which has not been proved to be a compound. This conception of an element comes to us

from Boyle (about 1661), and is a thoroughly scientific one. At present there are about seventy different elements known to chemists. It is quite possible, however, that some of these substances which we now class as elements under our definition may be proved by future research to be compounds. Still they are none the less elements for us in the meantime, in so far as our present knowledge is concerned.

The following list contains the names of sixty-eight elements which are definitely known to chemists—

Aluminium	Didymium	Molybdenum	Silver
Antimony	Erbium	Nickel	Sodium
Arsenic	Fluorine	Niobium	Strontium
Barium	Gallium	Nitrogen	Sulphur
Beryllium	Germanium	Osmium	Tantalum
Bismuth	Gold	Oxygen	Tellurium
Boron	Hydrogen	Palladium	Thallium
Bromine	Indium	Phosphorus	Thorium
Cadmium	Iodine	Platinum	Tin
Cæsium	Iridium	Potassium	Titanium
Calcium	Iron	Rhodium	Tungsten
Carbon	Lanthanum	Rubidium	Uranium
Cerium	Lead	Ruthenium	Vanadium
Chlorine	Lithium	Samarium	Ytterbium
Chromium	Magnesium	Scandium	Yttrium
Cobalt	Manganese	Selenium	Zinc
Copper	Mercury	Silicon	Zirconium

Several other substances are still under investigation as regards their supposed elementary nature, but their names are not in the meantime included in this list.

The elements are very commonly classed into **metals** and **non-metals**. The beginner should note, however, that this division is a purely artificial one, and that a sharp line of distinction cannot be drawn. For although a typical metal such as iron or sodium differs widely in its chemical characters from a typical non-metal such as oxygen or sulphur, still the two classes pass gradually into each other, and several elements (arsenic for

example) may be placed in either class. The following fifteen elements are those usually classed as non-metals—

Arsenic	Chlorine	Nitrogen	Silicon
Boron	Fluorine	Oxygen	Sulphur
Bromine	Hydrogen	Phosphorus	Tellurium
Carbon	Iodine	Selenium	

Of these arsenic and tellurium exhibit, to a considerable extent, some of the characters of metals.

The most important chemical characters of typical metals and of typical non-metals will be mentioned in Chapter XIII.

As we have already seen (p. 12) there are two ways in one or other of which the composite nature of a compound may be demonstrated, namely, by analysis and by synthesis. Processes of analysis do not necessarily involve in every case the separation in the *free* or uncombined state of the constituent elements of a compound. It is, in fact, only occasionally that the presence in a compound of a particular element is detected by separating that element from all the others. In a very large number of cases it is only necessary to show that a certain new compound can be obtained from the substance under examination, in order to prove that this substance must have contained a particular element. Thus, it is not easy to obtain from litharge the oxygen which it contains, as such, in the free state. A compound which is known to contain oxygen can easily be obtained from it, however, by the action upon it of a substance which is known not to contain oxygen. For example, when litharge is mixed with powdered charcoal and heated to bright redness in a crucible, metallic lead is left in the crucible, whilst carbonic oxide, a gas which is known from other experiments to consist of carbon and oxygen, escapes. Here the formation of carbonic oxide is an indirect proof of the existence of

oxygen in the litharge, since this result can be obtained by using charcoal, which is quite free from oxygen and from any of the compounds of oxygen. Or when litharge is heated in a glass tube and a current of pure hydrogen passed over it, lead and water are the products. The formation in this case of water, a compound of hydrogen and oxygen, is also indirect proof of the existence of oxygen in the litharge.

It is necessary to distinguish between *mixtures* and chemical compounds. This is usually a comparatively easy matter, although it is not invariably so. The formation of a chemical compound is attended by certain phenomena characteristic of the occurrence of chemical actions in general, which are not observed when mere mechanical mixtures are made. The most striking of these phenomena will be discussed in Chapter IV. It need only be added here that a mixture may contain two or more uncombined elements, or two or more compounds; or it may be made up partly of elementary and partly of compound substances.

CHAPTER III

CHEMICAL ACTION—GENERAL CONDITIONS

THE majority of chemical changes (that is, of changes which by processes either of synthesis or of analysis give rise to the formation of new substances, as explained in the preceding chapters) may be classified under a comparatively small number of important heads. Two of the most important and most commonly occurring kinds of chemical change are those which simply involve *combination*, or the formation of more complex out of simpler substances, and *decomposition* or the formation of simpler out of more complex substances. Cases of each of these two kinds of chemical change may advantageously be studied for the purpose of getting some insight into the extremely varying conditions under which different chemical actions take place; and further, of observing how one and the same chemical action may occur under totally different conditions.

An important condition necessary for the occurrence of combination is that the substances which are to enter into the action are brought into *contact* with each other. That tendency which many substances exhibit to combine together, and to which the name *chemical affinity* is given, only comes into play when the substances are brought within an immeasurably small distance from each other. Accordingly chemical changes in general go on more readily the more intimately the substances

which take part in the changes are brought into contact. For example, dilute hydrochloric or sulphuric acid is acted upon by zinc, hydrogen gas being liberated and zinc chloride or sulphate being formed in solution. By employing the zinc in comparatively large pieces a slow and steady current of hydrogen is obtained. If rapid evolution of hydrogen is desired, granulated zinc is employed, as in this case a much greater surface of the metal is exposed to contact with the dilute acid. If zinc in powder were employed the hydrogen would be liberated with very great rapidity owing to the enormously increased extent of metallic surface exposed to the acid.

Granulated zinc is prepared by pouring melted zinc in a fine stream from a height of several feet into a pail of cold water. Zinc can be obtained in powder by pounding it at the temperature of 200° in an iron mortar.

Another most important condition which affects the occurrence of chemical action in general is that of *temperature*. Mixtures may in many cases be made at the ordinary temperature, without combination occurring, of substances which readily combine when the temperature is sufficiently raised. For example, a mixture of hydrogen and oxygen in the proportions of two volumes of the former to one volume of the latter may be preserved for an indefinite period at the ordinary temperature without combination occurring ; but if an electric spark is passed through the mixture, if a lighted taper is applied to it, or if any part of it is by other means heated to a temperature above that of dull redness, combination, accompanied by an explosion, occurs and water is produced.

Chemical actions take place when a jet of coal gas[1] burns in the air. It is well known, however, that coal

[1] Note that coal gas is not a single substance, but consists of a highly complex mixture of gases; and that the coal gases manufactured in different localities differ widely from one another in composition.

gas does not take fire spontaneously at the ordinary temperature, but that it requires to be lighted. In order to light a jet of coal gas the temperature of the mixture of gas and air just above the burner must be raised to at least a moderately bright red heat—contact with a body heated merely to dull redness will not do.

In the case of a burning match or taper the flame is almost white hot, and its temperature is far above that of bright redness.

Experiment 7.—Heat one end of a poker or other bar of iron to bright redness; then, holding the red-hot end above the burner of a gas jet, turn the gas alternately on and off for a number of times. Observe that so long as the metal is bright red the gas is kindled; but that by cooling, a point is soon reached below which the metal, although still quite visibly red-hot even when viewed in daylight, is no longer sufficiently hot to raise the gas to the temperature necessary for combination to occur.

Experiment 8.—Repeat Experiment 7, only feeding the burner with hydrogen instead of with coal gas. Observe that the metal bar continues to kindle the hydrogen jet until it has almost ceased to appear visibly red-hot by daylight. Observe, however, that when this stage has been reached it is still quite visibly red-hot when viewed in the dark.

Cases illustrating the influence of temperature, and quite analogous to the instances already given, are those in which combination occurs at the ordinary temperature, but does not begin if the temperature is sufficiently lowered beforehand. For example, hydrochloric acid gas and ammonia gas combine readily at ordinary temperatures and form ammonium chloride; but at an extremely low temperature (below the liquefying points of both gases) the substances do not combine at all. The combination of these substances at ordinary temperatures is seen in the following experiment.

Experiment 9.—Dip a glass rod into strong solution of hydrochloric acid and hold it near an open vessel containing strong solution of ammonia. Observe that a dense white cloud is formed. This cloud consists of solid particles of ammonium chloride, and is produced by the combination of the hydrochloric acid gas and the ammonia gas given off from the respective solutions.

In many cases there is a limit of temperature above which combination will not take place between substances which would combine were the temperature below the limit. In intimate connection with this limit of temperature it must be mentioned that in the decomposition, by the action of heat, of an already formed compound, the latter must be heated to a definite temperature before decomposition begins. The necessary temperature is different in the cases of different substances. If two substances which would combine at a low temperature are heated, before being brought into contact with each other, to a temperature above that at which the compound producible by their union decomposes, it is plain that combination will not occur.

Numerous instances are known of substances which will only combine with each other when their temperature is kept within comparatively narrow limits—below the lower limit combination does not begin, and above the upper limit any of the compound already formed decomposes again. Mercury and oxygen furnish a good illustration of this. These two elements do not combine under ordinary circumstances of temperature; but when mercury is kept heated to near its boiling-point and a current of oxygen is passed over it, slow combination occurs and mercuric oxide is produced. At a temperature not far above that at which the mercuric oxide is formed, it decomposes again into mercury and oxygen. This decomposition has been seen in Experiment 5.

It must not be supposed that the combination of any elementary or compound substance with any other, can

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be made to take place by bringing the substances concerned into contact, under some particular condition of temperature; nor that all compounds already formed can be decomposed by simply heating them. There are many substances, elements as well as compounds, which do not, so far as we are aware, enter into combination with each other under any circumstances to form new compounds. There are also numerous cases like the following. A compound is known which consists of gold and oxygen, but there is not any known method by which gold and oxygen can be made to combine with each other directly—that is, without the intervention of other substances. The compound here referred to can only be obtained by an indirect method, and usually as the product of decomposition of a more complicated compound containing gold and oxygen along with hydrogen. Again, we know that quicklime is a compound which contains oxygen and a metal called calcium, because we can, by synthesis, obtain quicklime from these substances. We cannot, however, by any direct method, whether by the action of heat or otherwise, separate quicklime again into oxygen and calcium, although these elements can both be obtained from quicklime by roundabout processes.

Whilst the effect of an increase of temperature is frequently, as we have seen, to cause the decomposition of a compound substance, or to cause combination to begin in a mixture of substances which can be preserved at a lower temperature without combining, it must be borne in mind that similar effects can in certain cases be produced by other agencies, such, for example, as electricity or light; and that although the temperature is a most important condition modifying chemical change, the temperature at which a change occurs may also be greatly modified by other circumstances. For example, a piece of metallic iron does not under ordinary circumstances take fire and burn in the air. Iron can be

obtained, however, in the form of an extremely fine powder, and this powder if simply thrown into the air at once takes fire, combining with the oxygen of the air. The substance which reaches the ground is an oxide of iron. In this case the temperature at which combination begins is very greatly modified by the fineness of the iron powder.

The effect of *light* in producing chemical action is very important. A mixture of hydrogen and chlorine in equal proportions by volume can be preserved *in the dark* without any combination occurring. When a lighted taper is applied to the mixture, combination takes place with explosive rapidity, and hydrochloric acid gas is produced. If a cylinder containing a similar mixture is exposed to diffused daylight (not to direct sunlight) slow combination goes on until eventually the original gases have entirely combined to form the same new compound as before. If the direct rays of the sun or of a very bright light from an artificial source are allowed to fall upon a clear glass vessel containing such a mixture, instant combination occurs, accompanied by an explosion, exactly as if a lighted taper had been applied.

Cases of decomposition by exposure to light are numerous and often of great practical importance. A large number of compounds containing silver undergo decomposition, some of them with considerable rapidity, when exposed to daylight. Upon this property possessed by silver compounds many of the most important processes in photography depend.

Experiment 10.—Procure a piece of "sensitised albumenised paper," as employed by photographers. This paper is impregnated with certain compounds of silver which are sensitive to light. Expose a piece of this paper to bright daylight, taking care to protect a portion of it from the light by covering it with an opaque body such as a coin or a metal weight. Observe that

the exposed portion of the originally colourless paper soon assumes a dark purple brown colour, and that the portion which is protected from the light is quite unaffected. The darkening observed is due to decomposition of the silver compounds.

We are not able to obtain conveniently from hydrochloric acid the hydrogen and the chlorine of which it is composed by simply heating it. The acid can, however, be decomposed, and the hydrogen and the chlorine collected separately, by passing a current of *electricity* through its dilute aqueous solution (see p. 31 and Chapter XVII.).

An extremely interesting case of another agency by which decomposition may be brought about has been observed with regard to carbon bisulphide. The latter is a liquid obtained by the direct union of carbon and sulphur at a high temperature. When a small quantity of this liquid is enclosed in a tube along with a quantity of fulminate of mercury (a very powerfully explosive substance which is used in the manufature of percussion caps), it is found after the latter has been caused to explode, that the carbon bisulphide has been decomposed by the *shock* of the explosion into its constituent elements, carbon and sulphur.

Instances are known of substances which only combine when they are mixed and subjected to an increased *pressure.* For example, phosphuretted hydrogen and hydrochloric acid gases do not combine under ordinary atmospheric pressure, but when the pressure is very considerably increased they combine to form a white solid compound (compare Chapter XV.). Cases have also been investigated in which solid substances combine when subjected together to extremely high pressure. For example, iron and sulphur combine to form ferrous sulphide when they are mixed in a state of fine division and subjected to a pressure of 5000 atmospheres. Combination between iron and sulphur can also be

brought about by other influences. See, for example, Experiment 21.

A remarkable fact, for which no sufficient explanation is known, has been observed with regard to certain cases of combination and of decomposition, namely, that these actions only go on in presence of other substances which apparently do not themselves undergo any chemical change. For example, a mixture of carbonic oxide and oxygen in the proportions by volume of two of the former to one of the latter can, under ordinary circumstances, be ignited by contact with a lighted taper: combination occurs throughout the mixture, accompanied by a slight explosion, and carbonic anhydride is produced. If the mixed gases, however, are made absolutely free from any admixture of water vapour, then, on heating a portion of the mixture to whiteness by means of an electric spark, the gases in the *immediate* neighbourhood of the spark combine, but the change is not propagated throughout the mixture. Again, an aqueous solution of bleaching powder does not give off oxygen when heated alone, but if a small quantity of a particular oxide of cobalt (one of the compounds which oxygen forms with a metal called cobalt) is added to a hot solution of bleaching powder, oxygen is given off abundantly. In this way large quantities of oxygen can be obtained from bleaching powder. Apparently the oxide of cobalt can thus decompose unlimited quantities of bleaching powder solution, and it does not itself seem to undergo any change.

It has been observed that some highly porous substances possess the important property of absorbing large quantities of certain gases. Of these substances spongy platinum[1] and several varieties of charcoal are amongst the most important. The absorption of ammonia gas

[1] Metallic platinum is left behind in an extremely porous and spongy condition, when certain platinum compounds are carefully heated to redness.

by charcoal can be easily observed, and it forms a striking experiment.

Experiment 11.—Heat to redness (just before using them) some fragments of charcoal made from cocoanut shell, and introduce them into a tall tube containing ammonia and standing in a trough of mercury. Observe that the volume of the gas is rapidly diminished, a column of mercury—on the top of which the pieces of charcoal float—rising into the tube to take the place of the ammonia which is absorbed by the charcoal.

Spongy platinum has the property to a very marked extent of absorbing hydrogen and oxygen, and of causing them to combine within its pores to form water. In several other instances combination is brought about in mixtures of gases, with formation of new compounds, by passing these mixtures at low temperatures over spongy platinum or over particular kinds of charcoal.

Reference has already been made (p. 17) to conditions under which an explosion can be brought about in a mixture of hydrogen and oxygen, in the proper proportions by volume. It has been recently observed with regard to such a mixture enclosed in a sealed glass tube, that any particular part of the glass can be slowly heated to dull redness without an explosion occurring, although combination of a portion of the gases takes place with formation of water. The presence of certain substances, such as silver and platinum, enclosed in tubes along with the mixed gases, very greatly lowers the temperature at which combination with only a very slight explosion, or slow combination without any explosion, occurs. It has also been shown that the temperature at which an explosion of the mixed gases takes place is considerably lowered when the pressure of the gases is increased.

In concluding this chapter a few general statements may be added regarding the two important classes of chemical actions—combination and decomposition—of which it mainly treats. Chemical combination may take

place (*a*) between two or more elementary substances; (*b*) between two or more compound substances; or (*c*) between representatives of both elementary and compound substances, as shown in the following examples—

(*a*) Iron and oxygen combine to form one of the oxides of iron;
(*b*) Hydrochloric acid and ammonia combine to form ammonium chloride; and
(*c*) Carbonic oxide and oxygen combine to form carbonic anhydride.

Chemical decomposition may likewise take place with the formation as decomposition products (*a*) of two or more elements; (*b*) of two or more compounds; or (*c*) of both elementary and compound substances, as shown in the following examples of decompositions by the action of heat—

(*a*) Mercuric oxide is decomposed into mercury and oxygen;
(*b*) Calcium carbonate is decomposed into quicklime and carbonic anhydride; and
(*c*) Red oxide of lead is decomposed into litharge and oxygen.

In addition to these classes of chemical actions there are two other highly important classes, namely, *substitution* and *double decomposition*. These are treated of in Chapter XIX. The conditions affecting actions belonging to either of these classes, and other actions which do not fall within any of the classes here mentioned, are, in general, analogous to those described in this chapter as affecting combination and decomposition.

CHAPTER IV

CHEMICAL ACTION—CHARACTERISTICS

BEFORE looking at those special phenomena which characterise chemical action, reference must be made to a law which is of great importance not only in chemical science, but in all sciences which have to deal with material substances. This is the **law of the conservation of matter.** The result of all experience leads us to believe that in the various physical and chemical changes which substances undergo, there is neither increase nor decrease in the total quantity of matter which takes part in these changes ; that, in short, matter is neither created nor destroyed by any means which we can employ. The law of the conservation of matter simply sums this up in the statement that matter can neither be created nor destroyed. The truth of this law is generally accepted, and the law itself may consequently be used as the basis upon which to found other theories.

The law of the conservation of matter applies to cases of chemical combination, and it is found accordingly that the weight of any compound substance is equal to the sum of the weights of its constituents. Similarly, in cases of decomposition the sum of the weights of the products of decomposition is equal to the weight of the substance decomposed. Reasoning from this it follows that if any substance gains or loses weight this must be attributed to a gain or to a loss of matter. The recog-

nition of this important fact with regard to chemical phenomena may be said to date from the time of the early experiments of Black, published (in English) in 1756. It will be shown in Chapter VI. how important was the full appreciation of the same fact for the foundation by Lavoisier, in 1778-1783, of a theory of combustion which gave a sufficient explanation of all the observed phenomena. In connection with the law of the conservation of matter it is of interest to the student of chemistry to observe that, so far as is known, the total quantity of each of the elements that exists in the world (including all that is in combination as well as all that is in the free state) is constant.

When chemical combination occurs, the individual characteristics of each combining substance disappear, and the product obtained possesses its own special properties and chemical characteristics. A compound as a rule does not bear much (and only occasionally does it bear any) general resemblance in external physical features to any of the constituents from which it is produced; and, further, it possesses inherent physical and chemical properties which are entirely its own, and suffice to characterise it and to distinguish it from all other substances. Some of the physical features and properties of substances which are of special importance from a chemical point of view, and which serve for the identification of the substances, are the colour, density, crystalline form, hardness, solubility in various solvents, melting-point, and boiling-point.

Numerous instances of combination, which have already been mentioned, clearly illustrate this characteristic of chemical action. Thus, hydrogen and oxygen, which are both gases at the ordinary temperature, combine to form water, which is liquid at the ordinary temperature, and possesses other properties which do not in the least resemble those of either of its constituents. Again, the two pungent gases, ammonia and hydrochloric acid, com-

bine to form ammonium chloride, a white odourless solid substance, which is physically and chemically quite different from either of them (compare Experiment 9). The properties of a compound are thus not what might be conceived to be the mean or average of the properties of its constituents.

It may be said generally that the more widely the substances which combine to form a new compound differ from each other in chemical and physical characters, the less does the compound produced resemble either of them. For example, the liquid metal mercury and the colourless gas oxygen differ from each other in general and chemical characters as widely, probably, as any pair of elementary substances could conceivably differ. Mercuric oxide, the red solid substance which results from their combination, does not possess any external character suggestive of its containing either of them, and only operations involving chemical change reveal this fact concerning it. On the other hand, the yellowish gas chlorine and the dark coloured crystalline solid iodine—elementary substances which are chemically closely related to each other (p. 226), and exhibit many points of chemical resemblance—combine to form a reddish brown liquid which possesses properties somewhat remotely resembling those both of chlorine and of iodine. This liquid solidifies, forming very dark red crystals, which, however, melt at a temperature far below the melting-point of iodine (p. 6).

In the majority of cases in which chemical action occurs, and particularly in cases of chemical combination, heat is given out. This is notably the case, for example, when hydrogen and oxygen combine to form water.

Experiment 12.—Burn a jet of hydrogen gas. Observe that the flame is all but non-luminous. Hold a fine platinum wire in the flame, and observe that it is heated almost white hot.

Experiment 13. — Procure a piece of quicklime, place it in a dish and pour some water over it (use a little more than its own volume of water). Observe that in a short time the quicklime becomes very hot, cracks, swells up, and falls to a fine powder. The water acts chemically upon the quicklime, and during the action heat is given out.

Numerous cases of chemical action are nevertheless known, some of these also being cases of combination, in which heat is absorbed. For example, heat is absorbed when carbon and sulphur combine to form carbon bisulphide.

Besides these thermal changes, it is observed that chemical actions are also frequently accompanied by electrical and other phenomena. Thus the production of a current of electricity from certain forms of battery always accompanies a chemical change occurring within the battery to the materials of which it is constructed.

Chemical actions which occur with the evolution and with the absorption of heat have been called respectively exothermic and endothermic actions. It is most important to observe that the same exothermic chemical action can be carried out in different cases with the same quantities of the reacting substances, but with the conditions so altered that the same quantity of heat is not given out as such in each case. A portion of the obtainable heat may, for example, be transformed into electricity, as occurs in various forms of battery. This is illustrated by the following example: When zinc dissolves in dilute sulphuric acid, zinc sulphate is formed in solution and hydrogen gas is liberated. This change is accompanied by the giving out of heat, and the quantity of heat so given out can be measured. It is found that the same quantity of heat is given out in two or more different experiments, carried out under similar conditions when the same quantity of zinc is dissolved in each experiment. In some forms of battery

a current of electricity is produced by the action of dilute sulphuric acid on zinc—that is, by the chemical action we are just considering, but under a modification of the conditions.[1] Within the battery, while it is in action, some heat is given out, and the chemical change is identical with that already mentioned—zinc sulphate and hydrogen are formed, but instead of a part of the heat, as obtained under the former conditions, a current of electricity is produced. This current of electricity can be transformed back again into heat, and the quantity of heat obtainable from it is equal to the total quantity of heat obtainable by dissolving in dilute sulphuric acid the amount of zinc which dissolves within the battery, minus the quantity of heat which is actually given out in the battery. The current of electricity is not necessarily transformed into heat in the neighbourhood of the battery. It may be conducted by wires to a distance and there transformed.

We thus see that a current of electricity can be converted into heat. With proper appliances it is possible to convert heat into a current of electricity. Heat and electricity in motion are both forms of energy, and the maximum quantity of either which can be got from a definite quantity of the other is constant. These two forms are not the only ones in which energy may appear. We have, for example, radiant energy (light, heat radiation, chemical radiation); the energy of moving bodies (kinetic energy); and the energy of position or potential energy, of which chemical energy is a special case. All these forms are mutually convertible, although the ease with which the conversion may be effected differs greatly in different cases. For example, when a rifle is fired, the chemical energy of the gunpowder becomes transformed partly into light, partly into heat, partly into the energy of sound vibrations (moving particles of air),

[1] For the construction of a simple form of battery in which zinc and dilute sulphuric acid are employed, see Chapter XVII.

partly into the energy of the moving bullet. It is sufficiently plain that this transformation of energy cannot easily be reversed.

Energy is measured as far as possible in terms of work.

Like matter, energy can neither be created nor destroyed (compare p. 26). This statement is known as the law of the conservation of energy. It may be noted in this case, however, that the quantity of each of the ultimate forms of energy is not constant, but that all energy tends to become heat energy.

In many instances where chemical action takes place with the giving out of heat, the action is capable of being reversed. In such a case either the quantity of heat which was given out when the action took place must be supplied again in order that the action may be undone, or, to effect the same result, there must be supplied in some other form an amount of energy equivalent to this quantity of heat. Accordingly, when much heat is given out in any chemical action, much heat, or much energy in some other form, must be supplied in order to reverse the action. Hydrogen and chlorine, for example, combine to form hydrochloric acid gas under the circumstances described in the preceding chapter. Much heat is given out during the combination. Hydrochloric acid can be decomposed again into a mixture of hydrogen and chlorine by heating it sufficiently. The quantity of heat necessary to effect the decomposition is here simply supplied from an external source.

The decomposition of hydrochloric acid gas, by heating it, only begins at 1500°, and at a very high temperature it is not quite complete. On cooling again the mixed gases recombine completely (compare Chapter XV.).

When hydrochloric acid gas is dissolved in water, and a current of electricity is passed through the solution

so obtained, the acid is decomposed into hydrogen and chlorine; and by employing a suitable form of decomposition apparatus these two gases may be collected separately. This illustrates the transformation of electrical energy into potential energy (the chemical energy of the two gases). In the decomposition of the acid much energy is expended, just as much heat is given out during its formation by the combination of hydrogen and chlorine. Since hydrochloric acid is thus only decomposed into its constituent elements by supplying to it the necessary large quantity of heat, or of some other form of energy equivalent to this quantity of heat, it is regarded as a very *stable* compound. The idea of the stability of a compound is somewhat generally connected with its resistance to decomposing agencies, but the term itself is not employed in a very well-defined or strict sense. Thus, whilst hydrochloric acid is difficult to decompose by the effects of heat alone, it is easily decomposed even at ordinary temperatures by the action of zinc or of iron upon its solution in water—hydrogen being liberated whilst zinc chloride or ferrous chloride is formed in solution. During this action heat is given out.

In the case of chemical actions which take place with the giving out of heat, it very frequently occurs, when the action is once started in any part of a suitable mixture, that the heat given out during the combination of one part is sufficient to start the action in the surrounding parts; and so the change is propagated throughout the entire mixture. It is in this way that the explosive combination of a mixture of hydrogen and oxygen, or of a mixture of hydrogen and chlorine, or the firing of a train of gunpowder, is brought about. When the combination is once started in a part of the mixture, it is propagated with great rapidity throughout the whole, by reason of the fact mentioned above. Although in these instances the propagation of the change is rapid,

it is by no means instantaneous, since a very appreciable length of time is required for the explosion to travel along from end to end of a train of gunpowder a few feet in length. The rate of travelling differs very considerably in different kinds of gunpowder. The rate at which the explosion travels through a tube containing hydrogen and oxygen in the proper proportions is very much more rapid than that in the case of any kind of gunpowder. Dixon showed (1885) that the explosion travels through such a gaseous mixture at the rate of 2819 metres (about a mile and three-quarters) per second.

The propagation, in this way, of the chemical change throughout a mixture, in the proper proportions, of hydrogen and oxygen can be entirely prevented by the admixture in sufficient quantity of an inert gas—that is, of one which does not take any part in the chemical change. Such gas might be, for example, nitrogen, or it might be simply a great excess of hydrogen or of oxygen over the quantity required to convert the whole of the other gas into water. In a case of this kind it would appear that so much of the heat given out in the combination of one part of the mixture is used up in heating the admixed inert gas that the neighbouring portions are never raised to the temperature necessary for combination. Similar effects may be produced in other ways. For example, glass tubes containing explosive mixtures of hydrogen and oxygen can be heated to redness and sealed in the blowpipe, provided the part sealed is a thick-walled capillary tube. In this case combination does actually occur in that portion of the mixture which is contained in the capillary tube at the place heated, but the heat given out by its combination is so rapidly taken away to heat the walls of the cooler part of the capillary tube that neighbouring parts of the mixture are never raised to the temperature necessary for combination to begin. In the arrangement devised by Hemming for safely burning an explosive mixture of

hydrogen and oxygen to produce the oxyhydrogen blowpipe flame, the passage of an explosion backwards into the reservoir containing the mixed gases is prevented by causing the mixture to traverse (just before reaching the place where the combination is to occur) a piece of metal tubing tightly packed with fine copper wires placed longitudinally. This piece of apparatus constitutes simply a series of fine parallel capillary tubes, and in its effect in rapidly carrying off the heat it exactly resembles the capillary glass tube of the previous illustration.

A moderately thick iron wire can be made to burn in an atmosphere of oxygen. The iron combines with the oxygen to form an oxide, and the combination is accompanied by the giving out of so much heat that the oxide produced becomes white hot. This change will not continue to take place, however, in the air when a thick iron wire is used. The oxygen of the air is mixed with nearly four times its own volume of nitrogen, which, while it takes no part in the burning of the iron, has its temperature greatly raised, and in this way carries off so much of the heat that the action, even if begun in pure oxygen, soon comes to an end when the burning iron is withdrawn from the oxygen and placed in the air. It was stated, however, in the preceding chapter (p. 21), that iron in fine powder took fire spontaneously when thrown into the air, the difference in this case being due to the finer state of division of the iron. As illustrating an intermediate condition of matters it may be mentioned that when a *fine* iron wire is used, it can be made to burn in air for a short time in the same way that a thick wire can be burned in oxygen, only, of course, with much less brilliancy.

Experiment 14.—Procure some fine iron wire (not more than $\frac{1}{100}$ inch = 0·25 mm. in diameter). Rapidly heat an inch or so in length of this wire to bright redness in the flame of a Bunsen burner, and then hold it in the

air. Observe that the part of the wire which has been heated becomes almost white hot after its withdrawal from the flame, and that small globules of fused oxide of iron are formed, which, in some experiments, drop off. Observe also that the action is confined to that part of the wire which was heated in the flame, and that it soon comes to an end. (A thicker wire may be used in this experiment if a blowpipe flame is employed to heat it to bright redness.)

In cases where chemical combination is accompanied by the absorption of heat, the heat or other form of energy which is necessary in order that combination may go on must be supplied from some external source. For instance, carbon and sulphur vapour combine at a very high temperature to form carbon bisulphide, and during the combination heat is absorbed. In this case heat must be continuously supplied throughout the duration of the combination; because the heat required to raise further quantities of the elements to the temperature at which the action occurs, is not produced during the combination of the quantities which first combine. In short the action cannot be propagated in this way throughout the mass of the materials, and it ceases altogether as soon as the temperature, owing to the withdrawal of the external heat supply, falls below a certain point.

Heat is given out again when carbon bisulphide decomposes; and the same is the case also in the decomposition into nitrogen and oxygen of some of the oxides of nitrogen (nitrous and nitric oxides, and nitrogen peroxide); in the decomposition into chlorine and oxygen of the two oxides of chlorine (hypochlorous anhydride and chlorine peroxide), and in some other decompositions. In some of these instances, notably in those of the oxides of chlorine, the decomposition is extremely rapid and explosively violent, the heat given out by the decomposition of one part of the substance being suffi-

cient to raise neighbouring parts to the temperature of decomposition. In this way the change is spread throughout the whole of the substance. Compounds which are liable to sudden and violent decomposition are commonly called *unstable*. The quality of instability is very frequently observed in substances which give out heat during decomposition.

When chemical change occurs, the important characteristics as described in the foregoing are—

(1) The formation of new products, whether elementary or compound, which differ in physical and chemical properties from those which enter into the change; and

(2) A thermal effect, either the evolution or the absorption of heat, which accompanies the chemical change.

In addition to the above, there are fixed quantitative relations observed in the proportions to each other of the constituents of compounds, which are not observed in the case of mixtures. These cannot be discussed until the next chapter.

The occurrence or otherwise of the above two characteristics of chemical change, when substances are either simply mixed together or are mixed and subsequently subjected to new conditions, usually enables us to determine easily whether chemical change has taken place or not, and thus to distinguish between mere mechanical mixture and chemical combination. The weight of a mixture is, of course, equal to the sum of the weights of its ingredients, just as the weight of a compound is equal to the sum of the weights of its constituents (p. 26); but there is no thermal change observed when mere mixture takes place, and the properties of the mixture are simply made up *additively* of the separate properties of its ingredients; that is, the various properties of any ingredient are added on to those of all the other ingredients, and may be observed to a

certain extent in the mixture which is produced. Further, in the action upon it of various solvents, a compound behaves as a whole, while in a mixture each ingredient behaves in its own particular way; and hence by the use of appropriate solvents (as also frequently by other and purely mechanical means) the ingredients of a mixture may usually be separated more or less completely. Gunpowder furnishes a good example of a mechanical mixture. It is made by intimately mixing into a paste, along with water, appropriate quantities of charcoal, sulphur, and saltpetre (potassium nitrate) which have been previously reduced *separately* to very fine powder, and then drying the mixture at a low temperature. In its behaviour when fired, gunpowder exhibits characters which are made up additively of the individual characters of its ingredients. By treating gunpowder with water the potassium nitrate can be dissolved away from the charcoal and sulphur. The two latter ingredients can be separated by treating them with carbon bisulphide, in which liquid the sulphur alone dissolves. As examples of purely mechanical methods of separating from each other the ingredients of mixtures there may be mentioned the winnowing of chaff from grain; the sifting of the usually smaller seeds of weeds from relatively large seeds (as, for instance, in the case of flax seed, prior to sowing); and the process of gold washing, in which the heavier gold particles are roughly separated from particles of sand and earthy matter, the latter being got rid of by stirring up the mixture in a vessel through which a current of water flows.

It is not possible in every case to distinguish quite definitely a mixture from a compound. This is illustrated in the case of solution. Solutions in many respects behave exactly like homogeneous mixtures, but in others more like chemical compounds (see Chapter XVI.). A case in some respects analogous to those of solutions is that of the substance formed by the action of hydrogen

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on palladium. Palladium has the property of absorbing a large quantity of hydrogen. Under the most favourable conditions it absorbs nearly 1000 times its own volume of the gas. Up to a certain point a compound seems to be formed—beyond this the further absorption appears to be exactly like solution. The volume of hydrogen which is absorbed varies very greatly with the temperature, being greatest at about 90°, and it is also considerably influenced by the fineness of division of the palladium. The hydrogen seems to be held partly in true chemical combination and partly in solution.

CHAPTER V

LAWS OF CHEMICAL COMBINATION

WHEN chemical changes are studied from the point of view of the quantitative relations, by weight and by volume, of the materials which take part in them, a number of striking regularities are observed. The most important of these regularities are embodied in three laws, to which the following names have been given—

(1) The Law of Constant Proportions.

(2) The Law of Multiple Proportions (Dalton's law).

(3) The Law of Gaseous Volumes (Gay Lussac's law).

The discovery of these laws was of very great importance for the development of chemical theory, and the laws themselves must be considered here at some length. We shall discuss them successively in the order given above.

The law of constant proportions states that the same chemical compound is always composed of the same elements, and that these elements are always present in the compound in the same relative proportions by weight. For example, mercuric oxide consists of the elements mercury and oxygen only; and in any number of specimens of mercuric oxide these elements are combined in the proportions by weight of $12\frac{1}{2}$ parts of mercury to 1 part of oxygen. It follows from this that when mercuric oxide is decomposed by heating it (Experiment 5, p. 11) the quantities of mercury

and of oxygen produced in different experiments are proportional to the respective quantities of the oxide decomposed.

It must be borne in mind that the truth of the absolute accuracy of this law could only be established, if it were possible, by the elimination of all errors due to imperfections both of the methods and of the apparatus employed, to carry out quantitative experiments with rigid exactness. It may suffice to state here that the most careful and trustworthy experiments which we are able to carry out yield results which show extremely close, but not absolute, agreement with the law as stated. The differences which are observed are referred to errors of experiment. We may be able from time to time, by the employment of more accurate methods and more perfect apparatus, to diminish these errors, but we cannot eliminate them entirely.

It is of historical interest to note that about the beginning of the present century a prolonged controversy took place (from 1799 till about 1806) with regard to the question of constancy of composition of any chemical compound. This controversy was of great service to chemistry, by promoting the advance and increasing the accuracy of quantitative chemical analysis, which was then in a very backward state. The leaders on the opposing sides (C. L. Berthollet and Proust) were both eminent French chemists. Berthollet held that the composition of a compound was not rigidly constant, but that the relative proportions of the constituents might vary within moderate limits. This position he endeavoured to prove experimentally. Proust, on the other hand, held that the same compound always had the same quantitative composition, adducing his own quantitative analyses in support of his position, and pointing out that numerous substances examined by Berthollet were mixtures and not definite chemical compounds, and were on that account unsuitable substances to examine with a

view to settling the question at issue. As the result of the controversy Proust was eventually able to vindicate his position fully.

While the same chemical compound thus always consists of the same elements combined together in the same proportions by weight, many instances are known in which the same elements combine with each other in more than one proportion by weight, the resulting compounds in such cases being different substances, each of which possesses its own characteristic physical and chemical properties.

The law of multiple proportions states that when two elements combine with each other in more than one proportion by weight, the quantities of one of the elements which combine to form two or more compounds with a given quantity of the other element stand in simple multiple relations to each other. For example, mercury and oxygen form two different compounds, mercuric oxide and mercurous oxide. Each of these oxides possesses its own characteristic properties. In mercuric oxide the proportions by weight of the constituents are, as we have already seen (p. 39), $12\frac{1}{2}$ parts of mercury to 1 part of oxygen; in mercurous oxide the proportions are 25 parts of mercury to 1 part of oxygen; or there is just twice as much mercury in that quantity of mercurous oxide which contains a given weight of oxygen as there is in the quantity of mercuric oxide which contains the same weight of oxygen.

The law of multiple proportions was first established as a general law by Dalton, who, early in the present century (1803-1807), described a number of cases illustrating its truth. It is consequently often called Dalton's law of multiple proportions. The following are three of the cases which were known to Dalton. In carbonic oxide and carbonic anhydride the proportions by weight of carbon to oxygen (expressed in the simplest whole numbers) are respectively 3 to 4 in the

former and 3 to 8 in the latter. In marsh gas and olefiant gas the proportions by weight of carbon to hydrogen are respectively 3 to 1 in the former and 6 to 1 in the latter. In the three gaseous oxides of nitrogen the proportions by weight of nitrogen to oxygen (expressed in the smallest whole numbers) are respectively 7 to 4 in nitrous oxide, 7 to 8 in nitric oxide, and 7 to 16 in nitrogen peroxide.

It is very common to express the quantitative composition of a compound in parts by weight per cent. The simple multiple relations mentioned above are not perceptible when the compositions of the various compounds are thus expressed in parts by weight per cent; and it was only when Dalton calculated out the relative weights of one element which combine to form two or more compounds with one part by weight of another element that these relations became apparent. Thus 100 parts by weight of carbonic oxide and of carbonic anhydride consist respectively of carbon and oxygen as follows—

	Carbonic Oxide.	Carbonic Anhydride.
Carbon . .	42·86	27·27
Oxygen . .	57·14	72·73

From these data, which illustrate the form in which the results of quantitative analyses are ordinarily stated, we can calculate in the case of each oxide (I) the quantity of oxygen combined with one part by weight of carbon; or (II) the quantity of carbon combined with one part by weight of oxygen. The results of both of these calculations are given below—

I.

	Carbonic Oxide.	Carbonic Anhydride.
Carbon . .	1	1
Oxygen . .	1·33	2·67

II.

	Carbonic Oxide.	Carbonic Anhydride.
Oxygen . .	1	1
Carbon . .	0·75	0·375

Simple multiple relations in the proportions of the constituent elements are clearly shown in the results of both of these calculations, for 2·67 is practically twice 1·33, and 0·75 is twice 0·375. The relative proportions of carbon to oxygen in each of the two oxides (expressed in the smallest whole numbers) can easily be calculated from the numbers given either in I. or in II. These will be found to coincide with those already stated on p. 41. Similar multiple relations further illustrating the law are found in numerous other instances.

In order to explain these observed facts Dalton revived a very old idea, which is to be found, although altogether unsupported by any kind of experimental evidence, in the speculations of some of the ancient Greek philosophers; and thereby laid the foundation of what has become the so-called **atomic theory** in modern chemistry. According to the atomic theory matter of every kind is supposed to be made up of extremely small indivisible particles, which have been called **atoms**. These atoms are so small as to be

individually entirely beyond our powers of observation even with the aid of the most powerful magnifying instruments. We know nothing as to their shape, and only rough approximations can be made as to their size and weight. We know, however, that there are atoms of different kinds, and there are means of finding out their *relative* weights. The atoms of which each elementary substance is composed are supposed to be all alike, while in compounds, unlike atoms—that is, atoms of different elements—are supposed to be chemically combined with each other. Dalton's view was that the smallest conceivable particle of the most simply constituted compound must consist of two unlike atoms. He considered that carbonic oxide was such a simply constituted compound, and that the smallest particle of it consisted of one atom of carbon combined with one atom of oxygen. He knew, as we have already seen (p. 43), that in carbonic anhydride there is twice as much oxygen combined with a given quantity of carbon as there is in carbonic oxide, and his explanation of this fact was that the smallest particle of carbonic anhydride consisted of one atom of carbon combined with *two* atoms of oxygen. Again he considered nitric oxide to be a compound of the most simply constituted kind, and that the smallest particle of it consisted of one atom of nitrogen combined with one atom of oxygen. For reasons analogous to those just given in the cases of carbonic oxide and carbonic anhydride, he concluded that the smallest particle of nitrous oxide consisted of two atoms of nitrogen combined with one atom of oxygen, and that the smallest particle of nitrogen peroxide consisted of one atom of nitrogen combined with two atoms of oxygen. His views in this respect, so far as the oxides of carbon and of nitrogen are concerned, coincide with those held at present, although in some other cases his views are at variance with those now held.

According to the atomic theory the smallest conceivable particle of the most simply constituted compound must, as we have seen, consist of at least two unlike atoms. A somewhat more complex particle may consist of one atom of one kind and two of another, as in the cases of the particles of carbonic anhydride, nitrous oxide, and nitrogen peroxide, already mentioned (p. 44). Particles of much greater complexity than this are believed to exist in many substances. This part of the subject will be fully dealt with in Chapter XX. The smallest particle of any compound substance which is capable of a separate existence is necessarily an aggregate consisting of two or more atoms, and is called a **molecule** of that substance. An atom is, by definition, indivisible by any means, whether chemical or mechanical. A molecule is indivisible by mechanical means, but may be decomposed by chemical means. When a molecule is so decomposed by chemical means the products of its decomposition no longer possess the properties of the original molecule. A molecule may therefore be defined as the smallest particle of a substance which is capable of undergoing a chemical change.

From his quantitative analyses of a considerable number of substances Dalton endeavoured to determine the relative weights of the atoms of which he considered these substances to be composed. The original table embodying the results arrived at from his determinations constitutes the first attempt to tabulate the relative atomic weights of the elements (see Chapter XI.).

A most important distinction between compounds and mixtures may conveniently be pointed out at this place. In a compound the constituent elements must always be present in certain fixed and definite proportions which depend upon the number of atoms of each element present in a molecule of the compound. In a mixture, on the contrary, the ingredients may be present in any proportions, and these proportions can be altered at will.

The third law which has to be considered in this chapter is the **law of gaseous volumes.** This law states that when gases combine, the volumes of the gases which enter into combination are very simply related to each other and to the volume of the compound produced when the latter is a gas. For example, equal volumes[1] of ammonia and of hydrochloric acid gases combine to form ammonium chloride. The product in this case is a solid substance (compare Experiment 9). Also equal volumes of hydrogen and of chlorine combine to form hydrochloric acid gas; and the volume of the resulting gas is in this case equal to the sum of the volumes of its constituents. Again, two volumes of carbonic oxide combine with one volume of oxygen to form carbonic anhydride. In this case *contraction* takes place on combination, and the volume of the resulting carbonic anhydride is the same as that of the original carbonic oxide.

Gay Lussac and Humboldt were the first to observe these simple volume relations in the combination of gases. They showed in 1805 that one volume of oxygen combines with two volumes of hydrogen to form water. In the cases of numerous other gases which combine, Gay Lussac further showed, in 1808, the simple relations of the combining volumes, not only to each other, but also to the volumes of the resulting compounds when these are gases. For instance, he gave the case of carbonic oxide and oxygen, which has already been mentioned. A short time previously Amedée Berthollet had shown, by decomposition, that three volumes of hydrogen are combined with one volume of nitrogen in two volumes of ammonia gas. Gay Lussac made known (also in 1808) some other important observations on this subject. One

[1] In considering the law of gaseous volumes all gases are here regarded as being measured under such conditions that their volumes are comparable —that is, at the same temperature and under the same pressure (see Chapter VIII.).

of these was that when carbon or sulphur is burned in oxygen, the volume of the gas, after cooling, is found to be unaltered; that is, the volume of the carbonic anhydride, or of the sulphurous anhydride formed, is the same as that of the oxygen employed. Another interesting and most important observation was one respecting the relative volumes of nitrogen and oxygen which are combined with each other in nitrous and nitric oxides. Gay Lussac showed, by decomposition, that two volumes of nitrogen and one volume of oxygen are combined together in two volumes of nitrous oxide, and that one volume of nitrogen and one volume of oxygen are combined together in two volumes of nitric oxide. In other words, nitrous oxide contains its own volume of nitrogen and nitric oxide contains half its own volume of nitrogen. It is very important to compare this last observation by Gay Lussac of the relative *volumes* of the nitrogen and oxygen with the relative *weights* of the same elements present in these two oxides of nitrogen. The relative weights have already been given (p. 42) in illustration of Dalton's law of multiple proportions. In the table given below, the relative weights and the relative volumes are given side by side. In the columns headed "weight" there are given the weights of nitrogen and of oxygen contained respectively in 11 parts by weight of nitrous oxide and in 15 parts by weight of nitric oxide. In the columns headed "volume" there are given the volumes of nitrogen and of oxygen which can be obtained by the decomposition of quantities of the two oxides which yield the same volume of nitrogen—

	Nitrous Oxide.		Nitric Oxide.	
	Weight.	Volume.	Weight.	Volume.
Nitrogen .	7	2	7	2
Oxygen .	4	1	8	2

A brief consideration of the numbers given above shows that nitric oxide contains, for the same quantity of nitrogen, *whether by weight or by volume*, just twice as much oxygen as nitrous oxide does. It must suffice in this place simply to draw attention to this uniformity existing between the proportions by weight and by volume of the constituents of these gases. The importance of the fact that such uniformity does exist will be shown in Chapter X.

It may be pointed out here that Gay Lussac's law of gaseous volumes is quite in agreement with, and is indeed an important confirmation of, the law of constant proportions (p. 39).

The three following tables contain summaries showing the simple relations of the volumes of a few elementary and compound gases which enter into and are produced by chemical actions, and illustrate the most important points connected with Gay Lussac's law of gaseous volumes. All the volumes are expressed in litres (l.)

(1) In the following cases of combination, columns I. and II. give the volumes of the gases which combine, and column III. gives the volume of the compound, when gaseous.

TABLE I.

I. Combining Gases.	II. Combining Gases.	III. Compound Produced.
1 l. Hydrogen	1 l. Chlorine	2 l. Hydrochloric acid
1 l. Hydrochloric acid	1 l. Ammonia	— Ammonium chloride[1]
1 l. Carbonic oxide	1 l. Chlorine	1 l. Phosgene
2 l. Carbonic oxide	1 l. Oxygen	2 l. Carbonic anhydride
2 l. Hydrogen	1 l. Oxygen	— Water[1]

[1] Ammonium chloride is solid and water is liquid under ordinary circumstances. Reference is not made in this place to the volume which such sub-

(2) In the following cases of decomposition column I. gives the volume of the compound, and columns II. and III. give the volumes of the products of decomposition.

TABLE II.

I. Gas Decomposed.	II. Products of Decomposition.	III. Products of Decomposition.
2 l. Ammonia	1 l. Nitrogen	3 l. Hydrogen
2 l. Nitrous oxide	2 l. Nitrogen	1 l. Oxygen
2 l. Nitric oxide	1 l. Nitrogen	1 l. Oxygen
2 l. Nitrogen peroxide	1 l. Nitrogen	2 l. Oxygen

(3) In the cases of the following compound gases one constituent of each gas is a solid element. The volume of the compound gas given in column I. contains a quantity of oxygen, of hydrogen, or of nitrogen, which, in the free state, would occupy the volume given in column II.

TABLE III.

I.	II.
2 l. Carbonic oxide	1 l. Oxygen
2 l. Carbonic anhydride	2 l. Oxygen
2 l. Sulphurous anhydride	2 l. Oxygen
2 l. Sulphuretted hydrogen	2 l. Hydrogen
2 l. Marsh gas	4 l. Hydrogen
2 l. Ethane	6 l. Hydrogen
2 l. Cyanogen	2 l. Nitrogen

stances occupy *as gases*, since this subject can only be dealt with later (Chapter IX.).

CHAPTER VI

ILLUSTRATIONS OF CHEMICAL ACTION—COMBUSTION

THE familiar phenomenon of the burning of a candle is an example of a very large and important class of chemical actions which take place with the giving out of so much heat that the burning materials have their temperature raised to at least visible redness, and frequently to whiteness. The name **combustion** is commonly applied to such a chemical action. This name is an everyday, popular one which is not employed even by chemists in any strictly scientific sense; and there are numerous chemical actions, during the occurrence of which heat and light are given out, which are not cases of combustion in the popular sense. As an example of such a case it may be mentioned that when barium oxide is treated with water, combination takes place, and under the most favourable conditions the barium hydroxide produced may become red hot. The chemical change that occurs when an ordinary combustible substance burns in the air consists in the combination of the substance, or of some of its constituents, with the oxygen of the air. Boyle and other chemists of the seventeenth century were well aware that a combustible substance will not burn in absence of a continuous supply of air, but they did not know the true nature of the part which the air plays in the combustion.

Experiment 15.—Fasten a candle (or night light) upright in a shallow vessel containing water, in such a way that the water cannot reach the wick. Having lighted the candle, invert over the flame a glass bell jar or a large beaker, the mouth of which dips beneath the surface of the water and so encloses a quantity of air. Observe that in a short time the flame goes out. The length of time that the candle burns in the confined quantity of air depends upon the capacity of the inverted glass vessel.

The chief materials of which a candle consists are compounds containing carbon and hydrogen, or these elements along with oxygen. When a candle burns, the carbon and the hydrogen which it contains combine with the oxygen of the air to form carbonic anhydride and water respectively. Any oxygen which the materials of the candle contain goes so far towards the formation of these compounds. Evidence that these compounds are so formed can be obtained by the following experiments.

Experiment 16. — Invert a perfectly dry glass cylinder, open at one end, over a lighted candle. Observe that in a few seconds the inside of the cylinder becomes dimmed from the deposition upon it of minute drops of liquid. This liquid is water.

Experiment 17.—Allow a candle to burn as in Experiment 15 under a cylinder with a ground mouth, until the flame is just on the point of going out. Then remove the cylinder, pour into it some lime-water, close the open end by means of a glass plate and shake up. Observe when the lime-water is brought, by shaking, into intimate contact with the carbonic anhydride which the cylinder now contains, that a milkiness is produced in the lime-water owing to the formation of a white substance, calcium carbonate, which does not dissolve in water.

When a candle is burned in a confined quantity of

air, as in Experiment 15, its flame goes out while there is still a moderate proportion of unused oxygen present in the confined gaseous mixture. This is due to the fact that while combustion is going on, the proportion of oxygen to the other gases (the nitrogen of the air and the carbonic anhydride produced by the action, which are of no service in furthering the combustion) is steadily decreasing. These other gases at length preponderate to so great an extent in the mixture, and carry off so much of the heat evolved during the combustion, that the chemical change can no longer be propagated to new portions of the combustible material (compare the burning of iron in oxygen and in air, p. 34).

Substances which, like the wax of a candle, are themselves compounds containing two or more combustible elements, are frequently called **compound combustibles**. When they burn, both or all the combustible elements which they contain combine with oxygen if the supply of air is sufficient. If such compounds contain nitrogen, the latter either does not combine with oxygen at all during the combustion, or does so only to a very limited extent. In absence of a sufficient air supply, many combustible substances containing carbon and hydrogen (as for example the oil in a lamp) burn with a smoky flame. The production of such a smoky flame indicates that, for some reason, the air supply is insufficient to burn both elements, and as, in such a case, the hydrogen usually has the preference, some of the carbon escapes unburned as a black smoke.

As in the case of a candle, so also in the cases of coal, coal gas, wood, charcoal, paper, oils, and most of the combustible substances which are commonly burned as fuel or otherwise, the most important constituent elements of these substances are carbon and hydrogen; and the heat and light produced when they burn are the accompaniments of the chemical changes which go on

during the combination of these elements with atmospheric oxygen. There are, nevertheless, numerous other elements which are combustible in the popular sense—that is, they burn in the air, combining with the oxygen of the air to form oxygen compounds. Important examples of such elements are sulphur and phosphorus amongst non-metallic elements, and sodium, potassium, and magnesium amongst the metals.

Experiment 18.—Burn a small piece of sulphur in a deflagrating spoon (a small copper ladle attached to a copper wire). Observe the comparatively low temperature at which the sulphur takes fire, the pale blue, almost non-illuminating flame with which it burns, and the pungent smell of the gaseous product of the combustion. This product is sulphurous anhydride, one of the oxides of sulphur.

Experiment 19.—Burn a piece of magnesium wire or ribbon. Observe that the magnesium must be strongly heated before it takes fire; that, in burning, it gives out a brilliant white light; and that a white solid substance is produced as a result of the combustion. This white solid substance is magnesium oxide.

The student may further try for himself experiments similar to Nos. 18 and 19 with phosphorus, with sodium, and with potassium, noting the phenomena observed in each case. He should note particularly that dangerous accidents may occur through incautious handling of these three substances. Phosphorus must be preserved under water. When small pieces are required for use these should always be cut off under water, carefully dried between folds of filtering paper (in such a way that they are not rubbed), and then immediately made use of. Even with these precautions the pieces sometimes take fire in warm weather before they can be used for the purpose for which they are required. Special precautions must also be observed in preserving and handling sodium and potassium.

There are certain combustions which only require to be started in presence of air and do not then need any further external application of heat in order that the action may continue—provided there is a sufficient supply of air—until the whole of the combustible material is burned. These are illustrated by the burning of a wood or a coal fire, of coal gas, of a candle, of the oil in a lamp, etc., and are combustions in the popular sense of the word. There are numerous combustions, however, which do not continue to take place in air unless heat from an outside source is supplied during the whole action, although they do so continue in an atmosphere of oxygen free from the accompanying nitrogen of the air. For example, ammonia gas does not burn in air under ordinary circumstances, but burns if it is fed into a Bunsen burner along with coal gas; the heat given out in the combustion of the coal gas being sufficient to maintain a high enough temperature in the flame to burn the ammonia also. A jet of ammonia gas can, however, be lighted in a vessel containing oxygen, and will continue to burn as long as a sufficient supply of oxygen is maintained. When ammonia gas "burns," the hydrogen which it contains alone combines with oxygen. The nitrogen which it contains simply escapes as such in the uncombined state.

Iron furnishes another example which in its combustion resembles ammonia to a certain extent. It has already been stated (p. 34) that a thick iron wire continues to burn in pure oxygen when the combustion has once been started. On the other hand, if a similar wire is simply heated to redness in air, the atmospheric oxygen combines superficially with the iron, forming a thin layer of oxide, but the action does not proceed to the underlying portions of the metal, nor is it propagated to portions of the surface which have not been heated.

Experiment 20.—Keep a bar of iron at a bright

red heat for some time in a fire, and then allow it to cool. Observe that a brittle black scale, which can easily be detached, is formed upon the surface of the iron. This scale consists of an oxide of iron.

When any substance which burns readily in air is burned in pure oxygen, the combustion takes place with very greatly increased rapidity and brilliancy. The student should observe this for himself by filling several glass jars or bottles with oxygen, and burning in these a candle, a piece of charcoal, a piece of sulphur, etc. The effect of oxygen upon a glowing (but not flaming) piece of wood in causing it to burst into flame has already been observed, and employed as a means of testing for oxygen (Experiment 5).

The flame of a combustible substance is much hotter when the substance burns in oxygen than when it burns in air. The quantity of heat given out, however, is the same in both cases for equal quantities of the same substance burned, provided the same compound or compounds are produced in both cases. The reason for the hotter flame in the case of oxygen is that *in the same length of time* a larger quantity of the substance is burned, and consequently more heat is given out than when air is employed.

Just as there are combustions which take place in air or oxygen, so there are combustions in a wider sense of the word which do not require the presence of oxygen, but are still chemical combinations strictly comparable with ordinary combustions. Thus hydrogen and several other non-metallic elements, besides a large number of metals, burn readily in chlorine—some of them with great brilliancy, as, for example, phosphorus and antimony—a chlorine compound being formed in each case. Similarly numerous metals burn readily in sulphur vapour, as, for example, iron and copper.

Experiment 21.—Mix fine iron filings and flowers of sulphur in the proportions by weight of 2 parts of

iron to 1 of sulphur. Half fill a test-tube with this mixture and, having supported the tube in a suitable holder, apply heat to it by means of a Bunsen burner. Observe that when the mixture has become sufficiently hot, chemical action begins, and that combination takes place accompanied by the evolution of enough heat to raise the temperature of the product (ferrous sulphide) to redness.

Experiment 22.—Place some sulphur in a small flask and carefully heat it until it boils, and the flask has become nearly filled with deep brown coloured sulphur vapour. Then take a spiral of copper wire, heat one end of it, and lower it (hot end downwards) into the sulphur vapour. Observe that the copper at once begins to glow at the end which has been heated, and that this glow eventually traverses the whole length of the wire which is in contact with the sulphur vapour. The brittle black product of this combustion is cuprous sulphide.

There is an important class of combustible substances to which direct reference has not yet been made. It has already been stated (p. 51) that when a compound containing oxygen as well as carbon and hydrogen is burned, the oxygen which it contains is employed, so far, in the formation of carbonic anhydride and water. There are a few compounds which contain within themselves enough or nearly enough oxygen to convert the whole of their carbon and hydrogen into carbonic anhydride or carbonic oxide and water. These compounds, of which nitro-glycerine and gun-cotton are examples, are independent of an external supply of oxygen for their combustion, and when their combustion is once started they can then burn in an enclosed space to which oxygen has no access. In adjusting the quantities of sulphur, charcoal, and saltpetre which are to be mixed in order to make gunpowder, a sufficient quantity of saltpetre is employed in order to supply enough oxygen

to make the mixture independent of any external supply of oxygen for its combustion.

The chemical nature of combustion was not understood until the latter part of the eighteenth century. The older chemists supposed that when combustion took place a "fire material" made its escape from the burning substance, and that the ash, which in the cases of wood, coal, etc. remained behind, was the only portion of the original combustible substance which did not consist of this fire material. Such substances as wood and coal, which only leave a relatively small quantity of ash, were supposed to be much richer in this fire material than the combustible metals, which as a rule leave behind a relatively large quantity of a substance—the metallic *calx* of the older chemists—corresponding to the ash in the case of wood, etc. The so-called metallic *calx* of this period is now called a metallic oxide.

There would be a certain amount of plausibility about this early view of combustion, even to us, seeing how much of the substance of wood or of coal *disappears* on combustion, if we overlooked the fact, as the earlier chemists mostly did, that the products of combustion (which are, at first at least, mainly gaseous), if all collected, *weigh* considerably more than the combustible material burned. The formation of gaseous products of combustion was for a long time entirely overlooked; and, while a few of the chemists of the seventeenth and eighteenth centuries knew that when certain metals, such as tin, lead, etc. were burned, the substance produced weighed more than the metal employed, they did not then, as we do now, connect gain of weight with gain of matter, and so they were not in a position to make use of their knowledge of this fact, which was in reality one of the strongest arguments against their mistaken view as to combustion. Another important discovery was required in order to overthrow the old view and to

establish the present view instead. It was only after the discovery of oxygen by Priestley in 1774 and the observation that this gas was an ingredient of the atmosphere, that Lavoisier gave the true explanation of combustion as a chemical action in which the oxygen of the air takes part.

In connection with the subject of combustion some substances are commonly spoken of as "combustibles" and others as "supporters of combustion." The student must observe that these terms have reference to the circumstance that oxygen, which is necessarily present for ordinary combustions to take place, and is hence a so-called supporter of combustion, is a constitutent of the atmosphere, and as such is present in every space from which air is not specially excluded. If our atmosphere contained free hydrogen and no free oxygen, then oxygen would play the part of a combustible substance, since a jet of it would burn in the hydrogen of the atmosphere, and the latter would play the part of a supporter of combustion. As a matter of fact, in suitable forms of apparatus, a jet of oxygen can be made to burn in an atmosphere of hydrogen, of coal gas, or of sulphur vapour; or a jet of chlorine can be made to burn in an atmosphere of hydrogen, just as hydrogen, coal gas, or sulphur burns in oxygen, or as hydrogen burns in chlorine.

The fact that air is necessary alike for the combustion of the so-called combustible substances and for the support of animal respiration, drew attention at a comparatively early period to other resemblances between combustion and respiration. Several early experimenters knew, for example, that an animal cannot long survive if placed in a confined space to which fresh air is not admitted (just as a candle goes out under similar circumstances), and concluded that combustion and respiration were intimately related, long before the correct explanation of either had been given. Physiol-

ogists now regard the chemical changes which occur during respiration as akin to ordinary combustion, and the heat of animals as due to the chemical combination of the substance of the animal tissues with oxygen from the air.

CHAPTER VII

ILLUSTRATIONS OF CHEMICAL ACTION—OXIDATION AND REDUCTION

THE term **oxidation** is applied in a somewhat wide sense to those chemical changes which involve new combinations between elementary and compound substances and oxygen. The illustrations of combustion mentioned in the preceding chapter as taking place in air or in oxygen are examples of oxidation. In the changes which take place the combustible substances are **oxidised**, the products of the combustion being usually **oxides**. A considerable number of the elements combine directly with free oxygen to form such oxides. In a few cases this combination takes place at ordinary temperatures or on very gently heating, as, for example, in the cases of phosphorus, sodium, potassium, etc.; but the majority of the elements only combine with oxygen when moderately strongly heated, and some require to be raised to a very high temperature before combination begins. A few elements, such as chlorine, gold, platinum, do not combine directly with oxygen at all, although compounds of most of such elements with oxygen can be obtained by indirect methods (p. 20). Bromine and fluorine are the only two known elements of which oxides have not been prepared. Compounds are known, however, containing bromine and oxygen along with hydrogen,

but analogous fluorine compounds have not yet been obtained.

Numerous elements form compounds with oxygen in more than one proportion by weight, as has already been explained in discussing the law of multiple proportions (p. 41). In such cases the *lower* oxide, or oxide containing the smaller proportion of oxygen, is frequently capable of direct oxidation to form a *higher* oxide, or oxide richer in oxygen. This is illustrated by carbonic oxide which burns in air or oxygen, taking up just as much more oxygen as it already contains, and becoming oxidised into carbonic anhydride. Nitric oxide, again, combines with oxygen at ordinary temperatures to form nitrogen peroxide, and in doing so likewise takes up just as much oxygen as it already contains.

The oxides, or products of the combination of the elements with oxygen, are substances of great theoretical interest as well as of great practical importance. They exhibit amongst themselves striking differences in chemical characters, in accordance with which they may be divided into three distinct groups. The two most important of these groups are discussed from the point of view of these chemical characters in Chapter XIII. (p. 121).

Just as we have seen that a number of the elements combine directly with oxygen, so also a great many compounds undergo direct oxidation when exposed to the air at ordinary temperatures, or when heated in air or oxygen. Apart from cases of actual combustion, such as were dealt with in the preceding chapter, these actions as a rule proceed best in presence of water vapour or in aqueous solutions, and water, as well as the necessary oxygen, often takes part in the actions. Such oxidation may occur either to compounds which do not contain any oxygen, or to such as already contain some and are capable of combining with a further quantity. For example, if a clear solution of stannous chloride (a

compound containing tin and chlorine only) is exposed for some time to air, it absorbs atmospheric oxygen, and a white solid substance is precipitated which contains tin, chlorine, oxygen, and hydrogen. The hydrogen and a part of the oxygen are derived from the water of the solution. Again, if a solution of sodium sulphite is exposed to the air, it rapidly absorbs oxygen, and the sodium sulphite is converted into sodium sulphate. In undergoing this change the sulphite which already contains oxygen takes up more.

Experiment 23.—Procure some crystals of sodium sulphite and some of sodium sulphate; dissolve them in water separately, and test small portions of each solution as follows—

(1) Add dilute hydrochloric acid and shake up the mixture. Observe the pungent smell of the sulphurous anhydride, which is given off in the case of the sulphite but not in that of the sulphate.

(2) Add (to fresh portions) solution of barium nitrate, and then dilute nitric acid. Observe that in both solutions white precipitates are produced on adding the barium nitrate solution, but that in the case of the sulphite the precipitate dissolves completely in dilute nitric acid, while in the case of the sulphate it remains undissolved.

(3) Add (again to fresh portions) dilute solution of silver nitrate. Observe that a white precipitate is produced in the case of the sulphite, but not in that of the sulphate.

Then expose the two solutions to the air in open vessels for a week or so, and test them again as above. Observe that now the behaviour of the sulphate solution is the same as it was before, but that the behaviour of what was formerly the sulphite solution has become the same as that of the sulphate solution. (The solution of the sulphite may, of course, be tested at frequent intervals, and the progress of the change may thus be observed at various intermediate stages.)

Manganous hydroxide is a compound which very rapidly undergoes oxidation when placed in contact with

oxygen, and the action is accompanied by a change of colour.

Experiment 24.—Mix in a test-tube a solution of ammonia with a solution of manganous chloride or sulphate. Observe that a precipitate is produced which is nearly white; but that on standing, or much more rapidly on shaking up with the air of the tube, the precipitate gradually darkens and becomes eventually dark brown or almost black. The precipitate at first produced consists of manganous hydroxide, and the dark brown compound contains more oxygen than this hydroxide.

It often happens that only partial oxidation of a substance takes place when the source of the oxygen is air at ordinary temperatures, although the action would go further at a higher temperature. For example, sulphuretted hydrogen burns readily in the air, its hydrogen being oxidised to form water and its sulphur to form sulphurous anhydride. When the gas is dissolved in water, however, and the solution is exposed to the air, although oxidation likewise takes place in this case, the hydrogen alone is oxidised, while the sulphur separates in the solid form and settles down as a white deposit at the bottom of the liquid.

Experiment 25.—Place some clear aqueous solution of sulphuretted hydrogen in an open vessel and expose it to the air for a day or two. Observe that a deposition of white sulphur takes place, and that the solution loses its characteristic smell.

The change which occurs when the mineral called marcasite is exposed to atmospheric influences is an interesting case of oxidation. In this case the presence of water is necessary, and both moisture and oxygen therefore play important parts in the change. Marcasite is a compound of iron and sulphur (not the compound obtained as product in Experiment 21, but one relatively richer in sulphur than this), and one of the products

formed by its gradual oxidation in air is ferrous sulphate, a compound which contains iron, sulphur, and oxygen. But ferrous sulphate does not contain as much sulphur in proportion to the iron as marcasite does, and consequently there is more than enough sulphur entering into the reaction to form ferrous sulphate with all the iron concerned in it. This extra sulphur does not separate as such, but is converted into sulphuric acid, a compound which contains sulphur, hydrogen, and oxygen. The hydrogen and part of the oxygen which it contains are in this case derived from atmospheric moisture.

The process of oxidation by which ferrous chloride in solution in dilute hydrochloric acid is converted into ferric chloride, is an interesting and instructive one. Ferric chloride only differs in chemical composition from ferrous chloride by containing more chlorine for the same quantity of iron. Ferrous chloride alone cannot decompose hydrochloric acid, so that a mixture of these two substances in aqueous solution may be preserved unchanged for any length of time *out of contact with oxygen.* On exposing the mixture to air, however, oxygen is rapidly absorbed and ferric chloride is produced. The oxygen combines with the hydrogen of hydrochloric acid to form water, while the ferrous chloride combines with the chlorine to form ferric chloride.

Various cases of oxidations which occur at comparatively high temperatures, and with the giving out of much heat, have already been mentioned as illustrations of combustion. (See the preceding chapter, and compare also Experiment 4, in which melted lead is partially oxidised by exposure to air at the temperature of its melting-point.)

Since the atmosphere contains large quantities of free oxygen and also of water vapour, we might naturally expect to find, at the earth's surface at least, all

those substances which are capable of oxidation when exposed to atmospheric influences, either fully oxidised or undergoing gradual oxidation. This is indeed in accordance with actual observation. A number of the rocks which compose the earth's crust are already fully oxidised, and cannot therefore undergo any further change in this direction ; but in a very large number of cases the changes occurring to rocks at the earth's surface include oxidation as well as the chemical action of water and of carbonic anhydride, and the physical effects of rain, frost, etc. Oxidisable metals are not often met with in nature (in exposed situations at least) in the free or metallic state, but usually in combination as oxides or other compounds which do not undergo chemical change under atmospheric influences. Every one is familiar with the rusting to which iron is subject when exposed to the air, and with some of the modes of preventing it by suitably protecting the surface of the iron from the atmosphere, by painting or otherwise. The rusting of iron is a rather complex case of oxidation which requires the presence of carbonic anhydride and of water vapour, as well as that of oxygen. The reddish brown compound produced (rust) contains iron, oxygen, and hydrogen.

The processes of decay and putrefaction of the tissues of dead plants and animals are mainly due to oxidation ; the dead tissues becoming a complete prey to the action of atmospheric influences which they were able, to a very large extent at least, to resist so long as they formed parts of living bodies. The carbon and hydrogen which these substances contain are eventually oxidised, chiefly into carbonic anhydride and water respectively ; and their nitrogen is converted into ammonia.

Whilst free oxygen, as it occurs in the atmosphere, is the means by which oxidations are effected on the large scale by nature, or in most manufacturing opera-

tions which involve the combustion of any substance, whether as fuel or otherwise, there are also many operations carried out in chemical and other works and laboratories, in which oxidations are effected by making use not of free oxygen, but of *oxidising agents*. Such oxidising, or oxygen-yielding, agents are compounds containing oxygen, some or all of which they may give up to oxidise other substances. Nitric acid, chromic anhydride, hydrogen peroxide, and potassium nitrate, chlorate, and permanganate may be mentioned as examples of oxidising agents. These are all compounds rich in oxygen, and capable of giving up, under suitable conditions, a part of their oxygen to substances which are ready to combine with it. A solution of chlorine in water also acts as a powerful oxidising agent, and is employed as such in the process of bleaching various vegetable fibres, such as those of cotton and flax. In this process the chlorine combines with the hydrogen of some of the water, and the oxidisable colouring matter of the fibre combines with the oxygen.

When oxidising agents act as such by giving up their oxygen to other substances, they of course lose oxygen themselves, and are then said to be deoxidised or **reduced**. The process of **reduction** is thus the chemical reverse of oxidation, and simply consists in the removal of oxygen, by the action of some oxidisable substance, from compounds which contain it. Many of the ores of metals, or compounds from which the metals themselves are obtained, are simply metallic oxides; and the metallurgical processes by means of which the metals are obtained from these are cases of reduction. Just as there are oxidising agents possessing the characteristics that we have already mentioned, so there are also *reducing agents*, or oxidisable substances which are capable, under suitable conditions, of taking away oxygen from many substances which contain it. Carbon, carbonic oxide, hydrogen, and sulphuretted hydrogen

are examples of such reducing agents. A ferrous salt in solution, along with a suitable acid, also acts as a reducing agent. Of course, when reducing agents act as such, they themselves become oxidised.

When free oxygen effects an oxidation we cannot say that there is any simultaneous reduction, since there is no loss of oxygen sustained by any *compound* of that element; but when the oxidation is effected by an oxidising agent the latter suffers simultaneous reduction. Hence in all cases of the latter variety any illustration of oxidation is likewise an illustration of reduction, the two actions being mutual and interdependent. Some examples will make this quite clear.

When any oxide of lead is mixed with about one-eighth of its weight of charcoal, and the mixture is then heated in a crucible to bright redness, metallic lead is obtained by the reduction of the oxide, and can be poured out when the operation is finished; at the same time the oxygen of the oxide combines with the carbon of the charcoal to form carbonic oxide, which escapes as gas. Similarly if an oxide of lead or of iron is heated in a glass tube to dull redness, and a current of hydrogen is then passed over it, the hydrogen is oxidised to form water, and the oxide is reduced with the formation of metallic lead or iron. These cases, besides illustrating what has been said above about simultaneous oxidation and reduction, also illustrate the general conditions under which carbon and hydrogen act as reducing agents. Carbon usually acts at a bright red heat, and hydrogen at a somewhat lower temperature. Hydrogen, however, also acts as a reducing agent under other conditions at ordinary temperatures, as will be pointed out later in this chapter (p. 69).

Potassium nitrate and chlorate act with great readiness as oxidising agents. They part with their oxygen very rapidly and at a moderately low temperature to easily oxidisable substances, and in some cases cause

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combustions to take place with explosive violence. Potassium nitrate is the oxidising agent of gunpowder, and is largely employed in its manufacture. Potassium and other chlorates are similarly employed in the manufacture of fireworks. Chlorates part with their oxygen much more readily than nitrates do.

It is very common, especially in manufacturing operations, to regard cases of simultaneous oxidation and reduction as being examples of the one or the other of these chemical actions, from the point of view of the importance of the desired results to be attained. The beginner in chemistry must not be misled by this, which is really only a one-sided view of the chemistry of the actions. For example, in the smelting of iron, or reduction in the blast furnace of metallic iron from its ores, which usually consist largely of oxides, the reduction of the iron is the important metallurgical operation which the smelter has in view. From the point of view of the chemical actions concerned, however, this reduction is not more important than the simultaneous oxidation of part of the constituents of the coal employed in effecting the reduction. In this particular operation, the reducing agent which actually removes the oxygen from the oxides of iron appears to be carbonic oxide. This gas is produced in the blast furnace during the combustion of the coal. It then takes oxygen from the oxides of iron, reducing these to metal, and becoming itself oxidised to form carbonic anhydride.

While there are typical oxidising and reducing agents —the former containing oxygen, some or all of which they can give up to effect oxidation ; the latter either not containing oxygen and ready to combine with it, or already containing some and ready to combine with more —there are also a number of oxygen compounds which act as oxidising agents towards some reducing agents, and as reducing agents towards some oxidising agents. Chromic and sulphurous anhydrides are examples of such

substances. Solution of chromic anhydride when treated with peroxide of hydrogen becomes further oxidised; when treated with sulphurous anhydride it becomes reduced. Sulphurous anhydride in the last mentioned reaction (with chromic anhydride) becomes oxidised; by the action of sulphuretted hydrogen upon its solution it is itself reduced. In these last mentioned examples, and also in a great number of other cases, oxidation and reduction take place at ordinary temperatures and in aqueous solutions. Hydrogen can be made to effect reductions under similar circumstances by causing it to act in what has been called the *nascent state*. Treating the reducible substance with ready prepared hydrogen, at the ordinary temperature, is in most cases ineffectual in producing reduction; but this is effected if the reducible substance is introduced into the apparatus in which hydrogen is being liberated, say, by the action of zinc on dilute sulphuric acid. Some of the hydrogen in these cases is never liberated as such, but simply passes from the combined state as a constituent of one compound into the same state as a constituent of another. When nitro-benzene is treated in this way it is reduced to aniline; and ferric salts can in the same way be reduced to ferrous salts. Metallic zinc dissolves in dilute nitric acid, forming zinc nitrate, just as it dissolves in dilute hydrochloric or sulphuric acid, forming zinc chloride or sulphate. But in the case of nitric acid, hydrogen is not given off, and the endeavour has been made to explain this by the assumption that hydrogen in the nascent state acts upon the nitric acid, reducing it and being itself oxidised to form water. Various products of the reduction of the nitric acid may certainly be produced, the stage of reduction reached varying with the strength of the acid and the temperature at which the reaction takes place.

Sulphuretted hydrogen is a useful reducing agent, and frequently acts as such in solution by giving up its hydro-

gen to effect reduction, while its sulphur is precipitated. Its reducing action may be observed by mixing it with a number of substances in solution.

Experiment 26.—Add dilute hydrochloric acid and then solution of sulphuretted hydrogen to a solution of each of the following substances: (*a*) ferric chloride; (*b*) nitric acid (not too dilute); (*c*) potassium nitrite; (*d*) potassium chromate; (*e*) potassium permanganate. Observe that in each case a white precipitate is produced. Observe also the changes produced in the colours of the first and the last two of these solutions. The white precipitates consist of sulphur. The products of reduction cannot all be discussed here.

Similarly the oxidising action of potassium permanganate may also be observed on a number of substances in solution; the reduction of the permanganate being indicated by the disappearance of its purple colour.

Experiment 27.—To separate portions of a solution of potassium permanganate, mixed with dilute sulphuric acid, add solutions of: (*a*) ferrous sulphate; (*b*) sulphuretted hydrogen; (*c*) sulphurous anhydride. Observe that the intense purple colour of the permanganate disappears in each case, a colourless or nearly colourless solution being produced; and that in the case of the portion to which sulphuretted hydrogen is added, a white precipitate of sulphur is formed (compare Experiment 25). The products of oxidation cannot all be discussed here.

With regard to one of the actions in each of the two preceding experiments, some explanation may advantageously be given. The terms oxidation and reduction are occasionally used in a somewhat wide and loose sense. The conversion of a ferric salt into a ferrous salt is very commonly described as the reduction of the ferric salt, and the reverse action as the oxidation of a ferrous salt. The first of these actions, as it is illustrated in the case of Experiment 26 (*a*), is not really a case of reduction in the sense in which that term has already been em-

ployed, since it simply consists in the removal from ferric chloride of a part of the chlorine which it contains. Neither can the combination of the hydrogen of the sulphuretted hydrogen with this chlorine, to form hydrochloric acid, be regarded as a real process of oxidation. The whole reaction is analogous to, but strictly speaking is not, a case of oxidation and reduction. At the same time chlorine here plays a part quite analogous to that which oxygen plays in real cases of oxidation and reduction. The so-called oxidation of ferrous sulphate to form ferric sulphate, in Experiment 27 (*a*), may be regarded as consisting in the oxidation of the hydrogen of a portion of the sulphuric acid present, by means of oxygen from the potassium permanganate. It is thus the hydrogen of sulphuric acid which undergoes oxidation in this case. That part of the oxidised sulphuric acid which is not hydrogen, unites with the ferrous sulphate to convert it into ferric sulphate.

CHAPTER VIII

LAWS OF BOYLE AND OF CHARLES

WHEN a quantity of gas is confined under such circumstances that it is free to expand or to contract so as to occupy, owing to a change of conditions, a greater or a smaller volume, it is found that the volume which the gas occupies varies with change either in the pressure to which it is subjected or in its temperature. The amount of such variation is practically independent of the nature of the gas, being approximately the same for all gases, provided these are examined under conditions of pressure and of temperature such that they are far from their liquefying points, and provided also that very high pressures are not applied. The variations which are produced in the volumes of gases by changes of pressure and of temperature, within moderate limits, are in accordance with the following laws.

Boyle's Law.—When the temperature of a quantity of gas is kept constant, the volume which the gas occupies varies *inversely* as the pressure. Thus, supposing the temperature to be constant throughout, a quantity of gas which occupies 1 litre at a given pressure occupies half a litre when the pressure is doubled, one-third of a litre when the pressure is trebled, 2 litres when the pressure is diminished to one-half the original pressure, 3 litres when it is diminished to one-third, and so on. The pressure under which a gas is measured is, in the

case of low pressures, frequently expressed in "millimetres of mercury"—that is by the height in millimetres of a column of mercury which is supported by the pressure exerted by the gas. High pressures are often expressed in "atmospheres," and the average pressure of the atmosphere at sea-level ("one atmosphere") supports a column of mercury 760 millimetres high.[1]

In the accompanying figure (p. 74), A, B, and C represent successive stages of an experiment in which the volume occupied by the quantity of gas confined by a column of mercury in the closed limb of the tube may be observed: (A) at standard atmospheric pressure (760 mm.); (B) at twice this pressure; and (C) at three times this pressure. The extra pressure in B and C is produced by pouring mercury into the long open limb of the tube until the difference in mercury level in the two limbs is respectively 760 mm. and 1520 ($=760\times2$) mm.

E, F, G, and H similarly represent successive stages in an experiment, in which the volume occupied by the quantity of gas confined by a column of mercury in the closed limb of the tube may be observed: (E) at standard atmospheric pressure; (F) at one-half of this pressure; (G) at one-third of this pressure; and (H) at one-fourth of this pressure. The diminution of pressure in F, G, and H is produced by drawing off mercury from the open limb of the tube (by means of the stopcock) until the difference in mercury level in the two limbs is respectively 380 ($=760-760\div2$) mm.; 506·7 ($=760-760\div3$) mm.; and 570 ($=760-760\div4$) mm.

[1] Pressures are also frequently stated in "grams per square centimetre" and in "pounds per square inch" (the latter, in this country, in expressing the pressures inside steam boilers, etc.) The pressure of one atmosphere is equal to 1033 grams per square centimetre (a column of mercury of 1 square centimetre section and 760 millimetres high weighs 1033 grams), or to 14·7 pounds per square inch (a column of mercury of 1 square inch section and 29·92 inches (= 760 millimetres) high, weighs 14·7 pounds).

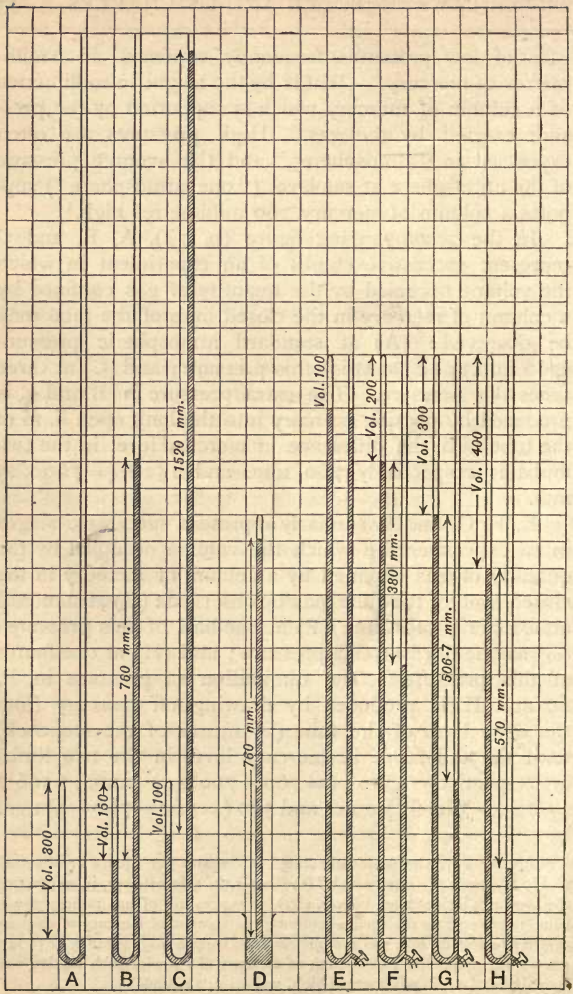
Vol. 800
Vol. 150
760 mm.
Vol. 100
1520 mm.
760 mm.
Vol. 100
Vol. 200
380 mm.
Vol. 300
906·7 m/m.
Vol. 400
570 mm.
A
B
C
D
E
F
G
H

FIG. 1.

D represents a barometer at its standard height (760 mm.).

From consideration of Boyle's law it is evident that the quantities of one and the same gas which, at constant temperature, occupy any given space under different pressures, are directly proportional to these pressures. Suppose, for example, 2 grams of a gas to occupy 2 litres at a given pressure, then 1 litre contains 1 gram of the gas. Suppose the pressure to be doubled, then the total volume of the gas is reduced to one-half its original volume, that is to 1 litre. 1 litre now contains 2 grams of the gas, or by doubling the pressure the quantity of gas contained in 1 litre has also been doubled.

Charles's Law.[1]—When the pressure to which a quantity of gas is subjected is kept constant, the volume which the gas occupies varies *directly* as the absolute temperature. The absolute temperature is obtained by adding 273 to the observed temperature, in degrees Centigrade, of the gas. Suppose that a quantity of gas occupies 273 cubic centimetres (c.c.) at 0°, and that it is maintained under constant pressure but is exposed to variations of temperature. The following table shows for the temperature given in column I. the corresponding absolute temperatures (column II.), and the respective volumes which the gas occupies at these temperatures (column III.).

I.	II.	III.
Temperature in °C. (=t).	Absolute Temperature (=273+t).	Volume in Cubic Centimetres.
0	273	273
1	274	274
2	275	275
10	283	283
30	303	303
− 1	272	272
− 10	263	263
− 30	243	243

[1] Sometimes called Gay Lussac's law.

Columns II. and III. show that the volume varies directly as the absolute temperature. A study of the numbers in columns I. and III. will also show that the volume which a gas occupies is increased or diminished by $\frac{1}{273}$ ($=0{\cdot}00366$) of its volume at 0° for each degree Centigrade through which the temperature of the gas is raised or lowered.

Note that if Charles's law held rigidly through wide ranges of temperature, a quantity of gas which at 0° occupies 273 c.c. when heated to 273° should occupy $273+273$ c.c.—that is its volume should be doubled. This is indeed approximately true. If it were possible to cool the gas to $-273°$ its volume should be reduced to $273-273$ c.c.—that is to nothing. The temperature of $-273°$ has never been reached, but we know that at attainable very low temperatures most gases become converted into liquids, and then cease altogether to obey Charles's law. There is evidence for the conclusion that all gases would similarly condense to the liquid state at temperatures above $-273°$, independent of the pressure. The temperature $-273°$ thus pointed to by the variations in the volumes of gases when cooled is of theoretical interest, and is called *absolute zero.*

Consideration of Charles's law shows that, when the pressure is assumed to remain constant, the quantities of one and the same gas which occupy a given space are inversely proportional to the absolute temperatures. Suppose, for example, that 2 grams of a gas occupy 1 litre at 0°, and that the temperature is raised to 273°. The absolute temperature is here doubled, and the volume, being directly proportional to the absolute temperature, is also doubled, or becomes 2 litres. 1 litre of the gas now contains only 1 gram, or the weight of 1 litre has been reduced to one-half by doubling the absolute temperature.

It still remains to consider the case in which the

volume of a quantity of gas is kept constant and the temperature is varied. In this case, which is affected by both of the preceding laws, the pressures are directly proportional to the absolute temperatures. Thus, for example, a quantity of gas occupies a given space at 0°. Its temperature is raised to 273°, but since its volume is kept constant, its pressure increases. According to Charles's law, if it were free to expand, its volume would be doubled at 273°. The pressure must therefore also be doubled in order to maintain it at its original volume; because this is, according to Boyle's law, the change of pressure which we should require to make in order to bring back the gas, at 273°, to the original volume which it had occupied at 0°, supposing it had been allowed in the first place to expand under constant pressure while its temperature was being raised from 0° to 273°.

Numerical Examples Illustrating these Laws.

(1) A quantity of gas measures 25 c.c. under a pressure of 780 millimetres of mercury. Required its volume when the pressure is diminished to 760 millimetres.

The new pressure is in this case $\frac{760}{780}$ of the original pressure. The volume of the gas varies, however, *inversely* as the pressure, and the new volume is therefore $\frac{780}{760}$ of the original volume or $25 \times \frac{780}{760} = 25{\cdot}66$ c.c. The volume is increased in the same ratio as the pressure is diminished.

(2) A quantity of gas measures 25 c.c. at the temperature of 27°. Required its volume when the temperature is lowered to 0°.

27° corresponds to $273 + 27° = 300°$ absolute.
0° ,, ,, 273° absolute.

The new absolute temperature is in this case $\frac{273}{300}$ of the original absolute temperature. The volume of the gas varies *directly* as the absolute temperature, and the new volume is therefore also $\frac{273}{300}$ of the original volume or $25 \times \frac{273}{300} = 22{\cdot}75$ c.c. The volume is diminished and the absolute temperature is lowered in the same ratio.

(3) A quantity of gas measures 25 c.c. under a pressure of 780 millimetres of mercury and at the temperature of 27°. Required its volume when the pressure is diminished to 760 millimetres and the temperature is lowered to 0°.

The effects produced upon the volume of a gas by variation of pressure and of temperature are independent of each other, so that the considerations applied to examples 1 and 2 may be applied in this case also; and the separate operations carried out in these examples may be combined in order to obtain the new volume in this case: thus, $25 \times \frac{780}{760} \times \frac{273}{300} = 23{\cdot}34 =$ volume in c.c. under a pressure of 760 millimetres and at 0°.

(4) At the temperature of 0° and under a pressure of 760 millimetres of mercury, 32 grams of oxygen occupy 22·33 litres. It is required to find the weights of oxygen contained in 22·33 litres under the new conditions below—

(*a*) at 0° and 780 mm.
(*b*) ,, 27° ,, 760 ,,
(*c*) ,, 27° ,, 780 ,,

The new weights are—

(*a*) $32 \times \frac{780}{760} = 32{\cdot}84$ grams.

(*b*) $32 \times \frac{273}{300} = 29{\cdot}12$,,

(*c*) $32 \times \frac{780}{760} \times \frac{273}{300} = 29{\cdot}88$ grams.

In order to be able to obtain a thorough grasp of the practical bearings of these laws, the student is strongly recommended to carefully study the foregoing examples, and also to work out the following exercises.

1. A quantity of gas measures 12 litres at 0° and 760 mm. Find its volume at 17° and 800 mm.

2. Find the volume at 0° and 760 mm. of a quantity of hydrogen which at −5° and 781 mm. measures 13·621 litres.

3. A quantity of gas measures 18 litres at 23·2° and 743 mm. Find its volume at 26° and 750 mm.

4. A quantity of gas occupies 10 litres at 740 mm. and 15°. What is its volume at 1000 mm. and −15°?

5. A quantity of hydrogen occupies 100 litres at 0° and 760 mm. Find the volume occupied on reducing the pressure to 740 mm. Find also the volume occupied when the same quantity of gas, at 740 mm., is heated to 15°.

6. A quantity of gas measures 100 c.c. at 0° and 760 mm. Find the value of x, under the new conditions, in each of the following cases—

	Pressure (mm.)	Temperature (°C.)	Volume (c.c.)
(*a*)	1000	0	x
(*b*)	725	0	x
(*c*)	760	7	x
(*d*)	760	12	x
(*e*)	760	x	120
(*f*)	x	0	105
(*g*)	x	10	100
(*h*)	x	10	110

7. A quantity of gas occupies the space of 1 litre at the temperature of 0° and under a pressure of 760 millimetres of mercury. Supposing its volume to remain constant it is required to find (*a*) its pressure when heated to 27°; (*b*) its temperature when it exerts a pressure of 800 millimetres.

Answers to the Foregoing Exercises.

1. 12·11 litres.
2. 14·259 litres.
3. 18 litres.
4. 6·629 litres.
5. 102·7 litres; 108·34 litres.
6. (*a*) 76 c.c.; (*b*) 104·8 c.c.; (*c*) 102·5 c.c.; (*d*) 95·6 c.c.; (*e*) 54·6°; (*f*) 723·8 mm.; (*g*) 787·8 mm.; (*h*) 716·2 mm.
7. (*a*) 835·2 mm.; (*b*) 14·4° (287·4° Absolute, and 287·4° − 273 = 14·4° Centigrade).

It has been stated that Boyle's law is only approximately true. For the majority of difficultly condensable gases the approximation may be regarded as very close for pressures below about 20 atmospheres. At pressures much above 20 atmospheres considerable deviations are observed, and the amount of deviation is different for different gases, as illustrated in the table given on the following page.

Deviations from Boyle's Law at High Pressures

(According to Natterer).

In the following table columns II. to VI. show how many litres of hydrogen, oxygen, nitrogen, air, and carbonic oxide can be compressed into the space of one litre by applying the pressures, in atmospheres, noted in column I. (counting the atmospheric pressure as the first atmosphere).

I. Pressure in Atmospheres.	II. Litres of Hydrogen.	III. Litres of Oxygen.	IV. Litres of Nitrogen.	V. Litres of Air.	VI. Litres of Carbonic Oxide.
1	1	1	1	1	1
10	10	10	10	10	10
100	98	100	99	100	100
200	181	198	190	191	193
300	258	287	271	276	281
400	333	372	334	346	361
500	395	439	379	394	411
600	454	482	415	433	447
700	505	517	446	463	478
800	548	547	475	487	504
900	587	572	499	508	525
1000	623	595	519	527	544

If Boyle's law held rigidly at high pressures, the figures in all the other columns would coincide with those in column I.

CHAPTER IX

DENSITY—VAPOUR DENSITY

By the density or absolute density of a substance is meant the number of units of mass of the substance which occupy unit space. We have already adopted the gram as unit of mass and the cubic centimetre as unit of space (see Introduction), hence, by the above definition, the density of a substance is the number of grams of that substance which occupy one cubic centimetre. Different substances possess very different densities, or, in other words, the quantities in grams of different substances which occupy one cubic centimetre differ widely. When any substance is free to expand and to contract, the volume which a given quantity of it occupies varies with variation of temperature; and hence the density of one and the same substance also varies with variations of temperature. In the case of gases, the amount of expansion or of contraction produced by raising or lowering their temperature through the same interval is practically the same for them all (see Chapter VIII.). In the cases of solids and liquids, however, the amounts of expansion or of contraction produced in different substances by similar changes of temperature, are not even approximately the same, but vary amongst themselves in an irregular manner. Water for example exhibits exceptional irregularities in the effect upon its volume of changes of temperature. Thus between its

freezing-point and 4° water contracts when heated and expands when cooled; while at temperatures above 4° it expands when heated and contracts when cooled. Any given quantity of water thus occupies at 4° a smaller space than at any other temperature; or at 4° a given space filled with water contains, at atmospheric pressure, the greatest quantity that it can contain. The temperature of 4° is hence called the *maximum density point of water*. At this temperature 1 gram of water occupies 1 cubic centimetre, and the density of water at this temperature is accordingly 1. At any other temperature the density of water is less than 1.

Water at the temperature of 4° has been adopted as standard of density, and the densities of other liquids and of solids as compared with this standard are called their **relative densities**. What are here called relative densities of substances are also very commonly called their specific gravities.

The subject of the relative densities of solids and of liquids need not be further discussed here, since the numbers representing them are not required in what follows. The methods by which they are determined, and other information regarding them, may be obtained from a text-book on natural philosophy. The relative densities of gases are, however, of great importance in chemical theory, and they must therefore be treated here with more detail.

In the case of gases another standard is adopted instead of water at 4° for the comparison of their relative densities. This standard is a gas, and sometimes air, sometimes hydrogen, is the one chosen. It has become more common recently to state the relative densities of other gases as compared with the density of hydrogen.

Under what have been called *standard conditions of temperature and of pressure*, by which are meant the temperature 0° and the pressure 760 mm., the absolute

density of hydrogen is 0·0000896. That is, 0·0000896 gram of hydrogen, at 0° and 760 mm., occupies the space of 1 cubic centimetre. This number illustrates the extremely inconvenient expressions that would be obtained for the relative densities of gases if these were uniformly compared with water at 4° as standard. In order to avoid the inconvenience that would thus arise, the density of hydrogen—the lightest known gas—has, as already stated, been pretty generally adopted as standard for the comparison of the relative densities of other gases; and 1 has been chosen as the number representing its density.[1] An important distinction between this standard and that adopted for the comparison of the relative densities of liquids and of solids is that it is not a standard *at any particular temperature*. We saw in the preceding chapter that the changes produced in the volume of a gas by changes of temperature and of pressure are independent of the nature of the gas, and are practically the same for all gases. It follows from this that the quantities of different gases which occupy any given space under the same conditions of temperature and of pressure must all vary in the same ratio with variations of temperature and of pressure; and therefore the relative densities of gases are independent of such changes, provided that the changes are the same for all the gases. It is not necessary then to compare the relative densities of other gases with the density of hydrogen under any *particular conditions* of temperature and of pressure, but only under the *same* conditions. In order to carry out the experimental determinations necessary to obtain the data for such comparison, several

[1] It is a matter of regret that the density of hydrogen is not chosen=2, instead of=1 as is usually the case. This standard number would be quite as useful as the one usually chosen, and its adoption would remove an altogether useless and unnecessary complexity (p. 92), which confuses beginners, and which they seldom fully understand. It seems to the authors that there is no reason why this very desirable change should not still be made.

methods are employed, two of which may be described here.

(1) A stout glass flask, of about 2 litres capacity, is employed. The neck of this flask is suitably fitted, so as to be air-tight, with a tube and stop-cock. By means of an air-pump the air is as completely as possible pumped out of this flask, the stop-cock is closed, and the flask is weighed empty. From the observed weight the true weight of the flask must be obtained.[1] It is then filled

[1] The observed weight as obtained by means of the balance is not the true weight of the empty flask. When any object is weighed in air its apparent weight is always, except in one particular kind of case, different from its true weight (and is usually less than its true weight), owing to the buoying-up influence upon the object of the surrounding air. The case in which there is no difference between the apparent and the true weights is that in which the counterpoising weights are made of the same material, or of material of the same relative density as the object which is being weighed. In such a case the volume, and necessarily also the weight, of the air displaced by the object to be weighed and that displaced by the weights is the same, and no error is introduced into the weighing. The amount of the error which is introduced in any other case is equal to the difference between the weight of the air displaced by the object and that of the air displaced by the weights. If the relative density of the weights is greater than that of the object, the apparent weight of the latter is too small by the difference in the weights of the quantities of air displaced; if the relative density of the weights is less than that of the object the apparent weight of the latter is too great by the same difference. In actual practice the error is a serious one when such a large object as a closed flask of 2 litres, or greater, capacity is concerned; and either a correction must be introduced in order to obtain as close an approximation as possible to the true weight, or means must be adopted to entirely eliminate the error. The correction may be made by finding the difference in volume of the air displaced by the empty flask and that displaced by the weights, estimating the weight of this quantity of air and (on the assumption that the relative density of the weights is greater than that of the empty flask) adding on the weight so obtained to the apparent weight of the flask. The error may be almost entirely eliminated by as nearly as possible counterpoising the flask to be weighed by means of another flask of the same size, and of known weight, and using only a few of the smallest weights to establish equilibrium in the balance. The volume of air displaced by the substances placed on each side of the balance is thus made practically the same. The error may be eliminated by weighing *in vacuo*; the whole operation of weighing being carried out in a space from which the air—the source of the error—has been removed.

with pure hydrogen, the temperature and the pressure being noted, and the true weight of the flask when filled with hydrogen is determined. The flask is afterwards similarly filled successively with other gases, the temperature and the pressure being noted in each case, and the weights likewise determined. From each of these weights the weight of the empty flask is deducted, and from the results so obtained the relative densities of the various gases, as compared with the density of hydrogen, can be calculated; for

$$\text{Relative density} = \frac{\text{Weight of contents of flask when filled at a given temperature and pressure with the gas of unknown relative density}}{\text{Weight of contents of flask when filled with hydrogen at the same temperature and the same pressure}}$$

If necessary, corrections are made for differences in the temperature and the pressure of the various gases, so as to make the observations comparable in every case. How these corrections are to be made may be ascertained from what has been stated in Chapter VIII.

(2) The second method for determining the relative densities of gases differs from that already described in so far that, for the purpose of weighing the gases, a small copper flask of about 160 cubic centimetres capacity, and capable of withstanding a high internal pressure, takes the place of the large glass flask. Into this flask the gas to be examined is pumped until the internal pressure is equal to from 20 to 25 times the atmospheric pressure. The weight of the flask and its contents is then determined, as in the first method. A portion of the compressed gas is allowed to escape into and fill a large measuring vessel of previously ascertained capacity, and the temperature and pressure are noted. It now only remains to find out by difference in weight how much of the gas has been drawn off from the copper

flask, and all the data are obtained for calculating the relative density as before.

Determinations of relative densities of substances in the gaseous state are not confined to those substances which are gases under ordinary conditions of temperature and of pressure, but may be made also in the cases of the vapours [1] of substances which are liquids or solids under these conditions. Such relative densities are commonly called the **vapour densities** of the substances. The vapour density of a substance may be determined according to one or other of two general methods. These methods consist in—

(1) Ascertaining the weight of a known volume, at known temperature and pressure, of the vapour of the substance.

(2) Ascertaining the volume occupied as vapour, at known temperature and pressure, by a known weight of the substance.

In actual practice vapour density determinations are now almost invariably made by Victor Meyer's method, which is founded upon the second of the above general methods, and is of general applicability through a wide range of temperature. In making a vapour density determination by this method, a small quantity of the substance to be examined is weighed off in a stoppered or sealed glass vessel of very small size. This vessel with its contents is then dropped to the bottom of a long tube (usually by means of a mechanical contrivance, so that it is not necessary to remove and replace the cork or stopper of the tube) the lower end of which has been previously raised to, and is maintained at, a temperature considerably above the boiling-point of the substance under examination. The substance becomes rapidly converted into vapour, and whilst this change is pro-

[1] Many substances which are solids or liquids at ordinary temperatures can be changed into the gaseous state, without undergoing decomposition, by having their temperature sufficiently raised. To the gaseous form of such substances the name *vapour* is usually applied by chemists.

ceeding, a quantity of air is driven, through a narrow side branch, out of the upper part of the long tube and is collected in a measuring tube over water. When the experiment is over, the volume of air so driven out is read off and also the temperature and the pressure at which it is measured. Subject to certain corrections, which need not be mentioned here, the volume of this air may be regarded as representing the volume which the quantity of substance taken for the experiment would occupy if it were possible to obtain it as gas at the temperature and pressure at which the air was measured, and it is so regarded in subsequently making the (comparatively simple) calculation of the vapour density. It will be observed that the data obtained in such an experiment include all that is required in the second of the general methods of vapour density determination as given above.

Vapour densities are strictly comparable with the relative densities of gases, and both sets of determinations are made for the same purpose. What this purpose is, will be shown in the next chapter.

It is stated in Chapter VIII. that the quantities of one and the same gas which at constant temperature occupy any given space under different pressures are directly proportional to the pressures (p. 75); and also that the quantities of one and the same gas which at constant pressure occupy any given space at different temperatures are inversely proportional to the absolute temperatures (p. 76). The subject of the densities of gases not having been discussed until the present chapter, it was not possible to explain what has now to be pointed out here as deducible from the above. This is, that when the temperature of a gas is kept constant, the absolute density varies directly as the pressure; and that when the pressure of a gas is kept constant, the absolute density of the gas varies inversely as the absolute temperature.

CHAPTER X

AVOGADRO'S LAW

IT was shown in Chapter V. that the volumes of gaseous substances which combine chemically stand in simple rational proportions to each other, and also to the volume of the substance formed, should it too be gaseous. But, according to Dalton's theory, the number of atoms of the various gases taking part in the chemical change must also be in simple rational proportions. Thus, if Dalton's view is correct that a molecule of nitric oxide consists of one atom of nitrogen and one atom of oxygen, and that a molecule of nitrous oxide consists of two atoms of nitrogen and one atom of oxygen, there must clearly be a simple and intimate relation between the volumes of gases and the numbers of atoms which these volumes contain ; for it has already been shown that two volumes[1] of nitric oxide yield on decomposition one volume of nitrogen and one volume of oxygen, and that two volumes of nitrous oxide yield on decomposition two volumes of nitrogen and one volume of oxygen (p. 47); or the separate volumes of the nitrogen and oxygen obtained as products of decomposition in each case, stand to each other in exactly the same ratio as the numbers of atoms of these elements in the respective oxides. It therefore

[1] It is assumed throughout this chapter that the volumes of all the gases mentioned in each illustration are measured under the same conditions of pressure and of temperature.

follows that some simple relation must subsist between the volumes of these gases and the number of atoms in them. The nature of the simple relation thus indicated was first pointed out by Avogadro. This Italian physicist endeavoured to explain Gay Lussac's observations on the combining volumes of gases (p. 46) by advancing in 1811 an hypothesis which (although almost unnoticed then, and for many years subsequently) has become within the last thirty years of great importance to modern chemistry. The form in which this hypothesis was originally given is almost identical with the following, which is the form now usually adopted in stating **Avogadro's law**:—

Equal volumes of gases, under the same conditions of pressure and of temperature, contain the same number of molecules. It may also be stated as follows:—

The numbers of molecules contained in different volumes of the same or of different gases are, under the same conditions of pressure and of temperature, directly proportional to these volumes.

Avogadro illustrated his hypothesis by means of various examples furnished by Gay Lussac's investigations, and showed that it was capable of explaining the observed facts in an extremely simple manner. In order to apply the hypothesis to several cases in which elementary gases enter into combination either with other elementary gases or with compound gases, Avogadro had to make a further assumption concerning the molecules of these gases. This further assumption was that the molecules of certain elementary gases, just like the molecules of compound gases, must consist, not of single atoms, but of groups composed of two or more atoms. This assumption, like the main hypothesis, remained practically in oblivion during several decades, and only attracted particular attention and assumed importance after the year 1856.

We shall examine some cases in which gases combine

to form new gaseous products, and shall observe the important conclusions which follow from the assumptions of Avogadro.

Two volumes of carbonic oxide combine with one volume of oxygen, and two volumes of carbonic anhydride are produced (Table I., p. 48), that is, three volumes of the uncombined gases contract on combination to form two volumes of the new compound gas; or the resulting carbonic anhydride occupies the same volume as the original carbonic oxide. The amount of the contraction which occurs on combination is equal to the volume of the original oxygen. According to Avogadro's hypothesis the number of molecules of carbonic anhydride produced is equal to the number of molecules of carbonic oxide employed, since the volumes are the same. But the molecules contained in the original oxygen are only half as numerous as those contained in the carbonic oxide, since the volume of oxygen employed is only one-half that of the carbonic oxide. Nevertheless each resulting molecule must partly consist of this oxygen, and as the carbonic anhydride molecules formed are twice as numerous as the oxygen molecules employed in their formation, each oxygen molecule must have been divided, and therefore must have consisted of not fewer than two atoms.

Again, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid gas. The volume of the resulting gas is thus equal to the sum of the original volumes. The number of molecules present in the resulting gas is therefore equal to the number of molecules in the uncombined gases; that is, the chemical combination does not in this case affect the number of molecules. The number of hydrochloric acid molecules, however, after the combination, is double that of the molecules in the original hydrogen. But each hydrochloric acid molecule contains some of this hydrogen. Hence each hydrogen molecule must

have been divided, and must therefore have originally consisted of not fewer than two atoms. By exactly similar reasoning it may be concluded that each chlorine molecule must likewise have consisted originally of not fewer than two atoms. From further considerations, which will be mentioned later (p. 99), there is evidence for the conclusion that molecules of oxygen, of hydrogen, and of chlorine each consist of two atoms.

In some cases of the combination of gases with each other, there is no reason to suppose that the molecules of an elementary gas have their component atoms separated and then redistributed so as to form essential portions of two new molecules. For example, one volume of carbonic oxide combines with one volume of chlorine to form one volume of phosgene. In this case it would appear (since the number of molecules in the resulting gas is the same as that in either of the original gases separately) that each chlorine molecule may simply be regarded as becoming added on to a carbonic oxide molecule, and that there is no need to assume the division of the chlorine molecules into their component atoms. The case of the formation of water vapour from its constituent elements also illustrates the same thing, besides illustrating the division of elementary molecules. Thus two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapour. In this case the number of water molecules produced is the same as that of the hydrogen employed, because the volume of the water vapour is the same as that of the hydrogen. There is therefore no need to assume the division of the hydrogen molecules. Since, however, there are only half as many oxygen molecules employed as there are water molecules produced, and since some of the oxygen enters into the composition of every water molecule, it is necessary to assume the division of each oxygen molecule. So far as the oxygen is concerned, this case is exactly parallel

with that of carbonic oxide and oxygen already described (p. 90).

The foregoing examples may serve to show how Avogadro's assumptions explain, in a simple manner, the volume relations of the gases entering into and produced by the reactions concerned. Other instances can also be as simply explained in an analogous manner; the observed facts being in complete accord with these assumptions.

If we now consider the relative densities of gases in connection with Avogadro's hypothesis it becomes evident, since equal volumes of different gases contain the same number of molecules, that the observed differences in weight of the same volume of different gases must be due to differences in weight of the individual molecules of which the gases consist. In short, we are led to the following as an alternative way in which Avogadro's law may be stated:—

Under the same conditions of pressure and of temperature, the molecular weights of gases are directly proportional to their densities.

From this it follows that the relative molecular weights of gases can be deduced from their relative densities. The relative densities of other gases are compared with the density of hydrogen taken = 1. Similarly the relative molecular weights of other gases are compared with the molecular weight of hydrogen taken as standard. But, for a reason which will be explained in the next chapter (p. 99), the molecular weight of hydrogen is chosen = 2, that is double the number representing its density. Hence the relative molecular weight of any other gas, whether elementary or compound, is represented by a number which is double the number representing its relative density.[1]

[1] If the density of hydrogen were chosen = 2 (instead of = 1) for the comparison of the relative densities of other gases, then the number employed to represent the relative density of any gas, whether elementary or compound, would also represent its relative molecular weight (cf. note on p. 83).

The following table gives (in round numbers) the relative densities and the relative molecular weights of some of the commoner elementary and compound gases.

	Relative Density.	Relative Molecular Weight.
Hydrogen . . .	1	2
Oxygen . .	16	32
Chlorine . . .	35·5	71
Nitrogen . . .	14	28
Carbonic oxide . .	14	28
Carbonic anhydride .	22	44
Marsh gas . .	8	16
Nitrous oxide . .	22	44
Nitric oxide . .	15	30
Ammonia . . .	8·5	17

This method of determining relative molecular weights is not restricted to substances which are gases under ordinary conditions of pressure and of temperature, but is also applicable to all those substances (solids and liquids at ordinary temperatures) whose relative densities in the form of vapour can be determined by the methods described in the preceding chapter. The relative molecular weight of the substance, in the form of vapour, is obtained by simply taking the number representing its vapour density and multiplying this by two.

While it is not possible to demonstrate the truth of Avogadro's law by any simple chemical experiment, we see from the simple explanation which it offers of many observed facts, that it possesses, even when viewed from the chemical standpoint only, a very considerable amount of probability. There are, however, numerous observations of physical facts which are in entire accord with it, and these bring so much additional evidence in its support as to make it rank as a demonstrated law.

CHAPTER XI

DETERMINATION OF ATOMIC WEIGHTS

WE have already seen in Chapter V. that, according to the atomic theory, every kind of matter is composed of atoms, and that these atoms are the smallest indivisible particles of elementary substances. It was stated in the same chapter that there are atoms of different weights, and further, that while the absolute weight of any atom can only be very roughly estimated, there are means of ascertaining the relative weights of the atoms of different elements, as compared with the weight of an atom of some element which is chosen as standard. It is the purpose of the present chapter to explain the most important methods of ascertaining the relative weights of the atoms of each different element. These weights are simply termed the **atomic weights** of the elements.

An atom of any element may be defined as the smallest portion of that element which is capable of entering into the composition of a molecule of any compound substance; and accordingly the atomic weight of an element, as defined above, is the relative weight of the smallest portion of it thus entering into the composition of a compound molecule, as compared with the assumed weight of the similar quantity of a standard element. It has been found that of all the known elements, hydrogen enters into combination in the smallest proportion by weight. The inference from

this is that hydrogen atoms are lighter than the atoms of any other element. The atom of hydrogen has therefore been chosen as standard for the comparison of atomic weights, and its weight is assumed equal to 1. It is important to note that hydrogen is quite arbitrarily chosen as standard with its atomic weight made equal to unity; and that any other element with any other assumed atomic weight might be so chosen. We shall see further on in this chapter that, for the practical purposes of *exact* atomic weight determination, another standard and another slightly different unit are in use at the present time.

In the previous chapter we learned that, if we accept the truth of Avogadro's law, we can explain the different relative densities of gases by referring these to differences in the weights of the individual molecules of different gases; and further, that the determination of the relative density of a gas leads us to its relative molecular weight. Now the weight of the molecule of a substance must be equal to the sum of the weights of all the atoms which the molecule in question contains, so that from the relative molecular weight and the quantitative composition of a compound substance, we might expect to get some information as to the smallest proportions by weight in which various elements enter into the composition of molecules—we might, in short, expect to get some information as to the atomic weights of the elements. This is as a matter of fact the most important way in which the atomic weights of the elements are approximately determined.

The following tables give the molecular weights and the quantitative composition of a number of compounds of the elements (I.) hydrogen, (II.) oxygen, (III.) carbon, (IV.) nitrogen, and (V.) chlorine, which will sufficiently illustrate the method of atomic weight determination that has been so far described above. The numbers given in the second column are obtained by

ascertaining in each case the weight in grams of the compound named which occupies in the gaseous state, under the same conditions of temperature and of pressure, the same space as 2 grams of hydrogen (p. 92): those given in columns III. and IV. are obtained from the quantitative analyses of the various substances.

I. Hydrogen Compounds.

I.	II. Molecular Weight.	The weight of compound in col. II. contains the following weights of	
		III. Hydrogen.	IV. Other Elements.
Hydrochloric acid .	36·5	1	Chlorine 35·5
Hydrobromic acid .	81	1	Bromine 80
Hydrogen	2	2	0
Water	18	2	Oxygen 16
Sulphuretted hydrogen	34	2	Sulphur 32
Ammonia	17	3	Nitrogen 14
Phosphuretted hydrogen	34	3	Phosphorus 31
Marsh gas	16	4	Carbon 12
Siliciuretted hydrogen	32	4	Silicon 28

II. Oxygen Compounds.

I.	II. Molecular Weight.	III. Wt. of Oxygen.	IV. Wt. of other Elements
Water	18	16	Hydrogen 2
Carbonic oxide . .	28	16	Carbon 12
Oxygen	32	32	0
Carbonic anhydride .	44	32	Carbon 12
Sulphurous anhydride	64	32	Sulphur 32
Sulphuric anhydride	80	48	Sulphur 32
Nitric acid	63	48	Hydrogen 1 Nitrogen 14

III. Carbon Compounds.

I.	II. Molecular Weight.	III. Wt. of Carbon.	IV. Wt. of other Elements.
Carbonic oxide . . .	28	12	16
Marsh gas	16	12	4
Ethane	30	24	6
Ethyl alcohol	46	24	22
Propane	44	36	8
Butane	58	48	10

IV. Nitrogen Compounds.

I.	II. Molecular Weight.	III. Wt. of Nitrogen.	IV. Wt. of other Elements.
Ammonia	17	14	3
Nitric oxide	30	14	16
Nitric acid	63	14	49
Nitrogen	28	28	0
Nitrous oxide	44	28	16

V. Chlorine Compounds.

I.	II. Molecular Weight.	III. Wt. of Chlorine.	IV. Wt. of other Elements.
Hydrochloric acid . .	36·5	35·5	1
Methyl chloride . . .	50·5	35·5	15
Chlorine	71	71	0
Hypochlorous anhydride	87	71	16
Ethylene chloride . .	99	71	28
Chloroform	119·5	106·5	13
Carbon tetrachloride .	154	142	12
Phosphorus pentachloride	208·5	177·5	31

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An inspection of the numbers contained in the third column reveals some striking regularities. Thus, in the quantity of each substance which in the state of gas occupies the same space, under the same conditions of temperature and pressure, as 2 grams of hydrogen (column II.), it may be observed that there is not contained in any case a smaller quantity of hydrogen than 1 gram, of oxygen than 16 grams, of carbon than 12 grams, of nitrogen than 14 grams, or of chlorine than 35·5 grams. Further, if the quantity of a compound as given in column II. contains more than 1 gram of hydrogen, it does not contain less than 2 grams; if more than 2 grams, not less than 3 grams, and so on. Similarly in the case of oxygen compounds, if the quantity as given in column II. contains more than 16 grams of oxygen, it does not contain less than 32 grams; if more than 32 grams, then not less than 48 grams, and so on. Regularities of exactly the same kind may be observed in the carbon, nitrogen, and chlorine compounds noted above. The lists of compounds given are intended to be merely illustrative and not exhaustive, since each table might have been greatly extended; and additional tables might have been given, including the compounds of many other elements. Had this been done, the same kind of regularities would have appeared throughout. In the case of each element, therefore, there appears a minimum number in column III., and all the numbers in this column for one and the same element are either this minimum number or multiples of it. It is concluded from the uniformity observed in this respect that the minimum number so obtained for each element represents (relatively to hydrogen as unity) the smallest proportion by weight in which that particular element enters into combination—in short, that this minimum number is the relative atomic weight of the element. The atomic theory evidently offers a sufficient explanation of the observed facts. We have

seen that in the oxygen compounds, for example, the molecular weights of these compounds are made up of the weights of the atoms of other elements present in the molecule besides oxygen, and of 1, 2, 3, etc. times the weight of one atom of oxygen. We may, it is clear, conclude from this that the various molecules contain 1, 2, 3, etc. atoms of oxygen. It is also clear that if a molecule contains any oxygen at all, it must contain not less than one atom of this element; if it contains more than one atom it cannot contain fewer than two atoms, and so on. Exactly similar considerations may be applied to the compounds of other elements.

In the tables, amongst the compounds of the elements hydrogen, oxygen, chlorine, and nitrogen enumerated, we have given the elements themselves. The student should note particularly that the quantity found in column III. in their case is *not* the minimum number representing the smallest weight which enters into their compounds, but is equal to twice this number. We are therefore led to conclude, that since their molecular weight is equal to twice their atomic weight as above determined, their molecules must each consist of two atoms.

It is, as we see, a matter of great practical convenience to have both atomic and molecular weights expressed in terms of the same unit, for then we have only to add together the weights of the atoms contained in the molecule in order to obtain the proper numerical value of the molecular weight. Now the atomic weight of hydrogen has already been chosen as unity, so that the molecular weight of hydrogen, which is equal to the sum of the atomic weights of the atoms in the molecule, viz. two atoms of hydrogen, must be $1 + 1 = 2$ in terms of this unit. This, then, is the reason why, in dealing with molecular weights, we always refer them to the molecular weight of hydrogen equal to 2 as standard, and not to hydrogen equal

to 1, as might at first sight appear more convenient (compare p. 92).

The conclusion that the minimum combining number of an element as determined from such tables as those on pp. 96 and 97 is the relative atomic weight of that element may not in all cases be justified. For it is plain that although the atomic weight of an element cannot be greater than the minimum quantity of it which enters into the composition of any molecule of its compounds, yet the atomic weight may be smaller than this quantity. We assume that the compound of any particular element which in the molecular weight (col. II. in tables) contains the smallest amount of this element only contains one atom of it in the molecule. This need not be so, however; the molecule might really contain, say, two atoms of the element, in which case we should estimate the atomic weight at twice its real value. When an element forms a great number of gaseous or volatile compounds, the chance of our making such a mistake is very small; but when, as is the case with many of the metals, only one or two volatile compounds are known, we are liable to commit this error. Of late years, however, other methods of determining molecular weights have been developed (compare Chapter XVI.), and these are applicable to substances in solution. Since every element forms a great variety of compounds soluble in water or in some other solvent, the number of compounds whose molecular weights we know is vastly increased, with the result that we may now determine atomic weights with practical certainty from molecular weights alone.

There is another method of atomic weight determination which has been very serviceable, being applicable to precisely those cases where the elements form no volatile compounds, and where the atomic weight therefore used to be doubtful. Dulong and Petit, in 1818, stated that the product of the atomic weight and the specific heat of solid elements is constant. This product

is called the **atomic heat**, so we may state the law as follows: The atomic heats of all solid elements are equal. The law is not perfectly accurate, as the atomic heats of the different elements vary somewhat; but they all approximate to the number 6·4, as the following table shows.

Element.	A Atomic Weight.	S Specific Heat.	A×S Atomic Heat.
Lithium	7	·94	6·6
Beryllium	9	·41	3·7
Boron (amorphous)	11	·25	2·8
Carbon (diamond)	12	·14	1·7
Sodium	23	·29	6·7
Magnesium	24	·245	5·9
Aluminium	27	·20	5·4
Silicon (crystalline)	28	·16	4·5
Phosphorus (yellow)	31	·19	5·9
Sulphur (rhombic)	32	·18	5·7
Potassium	39	·166	6·5
Calcium	40	·170	6·8
Scandium	44	·153	6·7
Chromium	52	·100	5·2
Manganese	55	·122	6·7
Iron	56	·112	6·3
Cobalt	59	·107	6·3
Nickel	59	·108	6·4
Copper	63	·093	5·9
Zinc	65	·093	6·1
Gallium	70	·079	5·5
Arsenic (crystalline)	75	·082	6·2
Selenium (crystalline)	79	·080	6·3
Bromine (solid)	80	·084	6·7
Zirconium	91	·066	6·0
Molybdenum	96	·072	6·9
Ruthenium	102	·061	6·2
Rhodium	103	·058	6·0
Palladium	106	·059	6·3
Silver	108	·056	6·0
Cadmium	112	·054	6·0
Indium	114	·057	6·5
Tin	118	·054	6·5
Antimony	120	·052	6·2
Tellurium	125	·047	5·9

Element.	A Atomic W	S ht. Specific Heat.	A×S Atomic Heat.
Iodine	127	·054	6·8
Lanthanum	138	·045	6·2
Cerium	140	·045	6·3
Tungsten	184	·033	6·1
Osmium	191	·031	6·2
Iridium	193	·0324	6·3
Platinum	195	·032	6·3
Gold	197	·032	6·3
Mercury (solid)	200	·032	6·4
Thallium	204	·0335	6·8
Lead	207	·031	6·4
Bismuth	209	·030	6·3
Thorium	232	·0276	6·4
Uranium	239	·0276	6·6

The elements which form marked exceptions to the law, having much too small atomic heats, are all elements with low atomic weights, and, with the exception of beryllium, form many volatile compounds, so that their atomic weights were never really in doubt. As the elements in the table are arranged in the order of their atomic weights, the prominent exceptions occur amongst the first eight elements.

When an element exists in more modifications than one, the specific heats of these may be somewhat different; for instance, carbon in the form of diamond has not the same specific heat as carbon in the form of graphite. It is therefore uncertain which form we ought to regard in fixing the atomic weight. Another source of uncertainty is the variation of the specific heat with the temperature. As a rule, the specific heat increases slightly with rise of temperature, but in the case of some elements the increase is very marked. Boron, carbon, silicon, and beryllium are such elements, and it will be noticed that these are the elements with abnormally small atomic heats. A few numbers illustrating this exceptional behaviour are given in the following tables.

BERYLLIUM.

Temperature.	Specific Heat.	Atomic Heat.
23°	·397	3·62
73°	·448	4·08
157°	·519	4·73
257°	·582	5·29

CARBON.

Diamond.			Graphite.		
Temperature.	Specific Heat.	Atomic Heat.	Temperature.	Specific Heat.	Atomic Heat.
−50°·5	·0635	·76	−50°·3	·1138	1·37
+10°·7	·1128	1·35	+10°·8	·1604	1·93
85°·5	·1765	2·12	61°·3	·1990	2·39
206°	·2733	3·28	202°	·2966	3·56
607°	·4408	5·3	642°	·4454	5·35
806°	·4489	5·4	822°	·4539	5·45
985°	·4589	5·5	978°	·4670	5·5

A consideration of these numbers shows that there is a tendency for the specific heat to reach a certain limiting value as the temperature rises, and that the atomic heat corresponding to this value approaches the normal atomic heat of 6·4. It will be noticed, too, that the specific and atomic heats of diamond and graphite, which are quite different at low temperatures, become above 600° practically identical.

In order to find an atomic weight by means of Dulong and Petit's law, we divide the number 6·4—the mean atomic heat—by the specific heat of the solid element. The quotient is not an exact atomic weight but only approximate, for the law is only approximately true; but taking into consideration the results of quantitative analysis, we can easily find the true atomic weight. For example, the specific heat of silver is ·056; if we divide 6·4 by this number, the quotient is 114. But we know that the exact quantity of silver that combines with one gram-atom (35·45 grams) of chlorine

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is not 114 grams, but 107·94 grams. We therefore take the atomic weight of silver as 107·94, and the product of this number with the specific heat, ·056, makes the atomic heat equal to 6·0, diverging slightly from the mean 6·4. To take another example: Mercury forms two compounds with chlorine, mercurous chloride and mercuric chloride. In the first compound 200 parts of mercury are combined with 35·5 parts of chlorine; in the second compound only 100 parts. We might therefore be in doubt as to the atomic weight of mercury. A consideration of the specific heat of the element settles the matter. The specific heat of solid mercury is ·032. On performing the division $6·4 \div ·032$, we obtain 200 as the answer: 200 is therefore the atomic weight of mercury. Vapour density determinations confirm this number.

The last example indicates to us that the problem of fixing an atomic weight may consist in determining which of several numbers arrived at by quantitative synthesis or analysis should be adopted as the real atomic weight. The numbers obtained from analysis are far more accurate than those determined from the specific heat or from the vapour density, and are therefore always used as the atomic weights once it is settled which of them is to be chosen.

Other methods besides those mentioned above have been employed for choosing the correct atomic weights. General chemical analogy between elements, and isomorphism, *i.e.* similarity of crystalline form exhibited by themselves or by corresponding compounds, were at one time of importance, but are now entirely superseded. The periodic arrangement of the elements (see Chapter XXI.) has also afforded valuable information in doubtful cases.

From what has been said the student has no doubt perceived that the determination of an exact atomic weight involves two distinct problems. An approximate

atomic weight for an element may be obtained from the approximate molecular weights of its compounds (as given by the vapour density or any of the more recent processes), or from Dulong and Petit's law. But there still remains the determination of the number which expresses the accurate atomic weight. This number is found by processes of synthesis or analysis involving the element or its compounds. What has to be determined is the exact proportion by weight in which it combines with other elements whose atomic weights are known. All exact atomic weights are now given as multiples of a unit such that the atomic weight of oxygen in terms of this unit is 16 exactly. The advantage of thus choosing oxygen as the standard consists in the fact that in practice the atomic weights of the elements are determined with reference to oxygen, or to some element whose atomic weight with reference to oxygen is known with great accuracy. Hydrogen was formerly made equal to 1 exactly, but this standard is practically inconvenient, because we do not know the relation between the atomic weight of hydrogen and those of the other elements with any great degree of exactness. The atomic weight of hydrogen, when that of oxygen = 16·000, is about 1·008, so that it does not differ much from unity; and in using round numbers, as we have done for the most part in this book, it makes no difference whether we take oxygen = 16·000 or hydrogen = 1·000 as standard.

The following example from the work of Stas may serve to show the degree of accuracy with which it is possible to determine atomic weights. Silver chlorate when heated gives off oxygen, and silver chloride remains behind. The chloride contains for each atom of silver one atom of chlorine: the chlorate has in addition three atoms of oxygen. By determining the weight of oxygen given off from a weighed quantity of chlorate, we can evidently compare the atomic weight of oxygen

with the sum of the atomic weights of silver and chlorine. Stas found that—

Silver Chlorate.	Silver Chloride.	Oxygen.	Sum of at. wts. of Silver and Chlorine.
138·7890 g. gave	103·9795 g. and	34·8095 g.	whence 143·3808
259·5287 g. gave	194·4435 g. and	65·0852 g.	whence 143·4011
		Mean	143·3940

Further, Stas synthesised silver chloride by burning silver in chlorine gas. His numbers were—

Silver.	Silver Chloride.	At. wt. of Silver.
91·462	121·4993	107·9439
69·86735	92·8145	107·9417
101·519	134·861	107·9414

From these experiments the quantities of the silver and the chlorine separately can now be compared with the quantity of oxygen in the chlorate, and thus we may obtain the atomic weights of silver and of chlorine. The atomic weight of silver arrived at in this way by three experiments is given in the third column. Working by five quite different methods, Stas obtained the following numbers for the atomic weight of silver—

I. 107·9401
II. 107·9406
III. 107·9233
IV. 107·9371
V. 107·9270

It is practically certain that the number 107·94 expresses the atomic weight of silver, referred to oxygen = 16·000, with an error of only about a unit in the last decimal place.

CHAPTER XII

CHEMICAL NOTATION—SYMBOLS, FORMULÆ, AND EQUATIONS

In the preceding chapters a considerable number of numerical matters relating to chemical composition and chemical action have been dealt with. Of these there may be mentioned here, as of importance for the subject of the present chapter—the relative atomic weights of the elements; the laws of constant and of multiple proportions; the law of volumes; Avogadro's law; the relative densities of gases and vapour densities; and the relative molecular weights of compounds. In order to be able to represent concisely the chemical composition of compounds; to express symbolically some of the other numerical facts concerning them; and to give a short and accurate account of definite chemical actions, chemists have devised, and constantly employ, a system of notation which it is essential that the beginner should fully understand, and be able to use with facility.

As a means of shortly representing its written name each element has had assigned to it a **symbol**. The symbol for an element simply consists, in several cases, of the first letter of the name of the element. For example, H is the symbol for hydrogen, N that for nitrogen, O that for oxygen. In a number of cases there are several elements whose names begin with the same letter; and when this occurs, the first and a

succeeding letter are used collectively as the symbol for each element, except that occasionally the simple initial is reserved for a specially important element. Thus C is the symbol for carbon, while those for the other elements whose names begin with C are respectively Cd (cadmium), Cs (cæsium), Ca (calcium), Ce (cerium), Cl (chlorine), Cr (chromium), Co (cobalt), Cu (copper). The symbols for a few of the elements are derived from the Latin (or Latinised) names for these elements, as follow: Sb for antimony (*stibium*), Cu for copper (*cuprum*), Au for gold (*aurum*), Fe for iron (*ferrum*), Pb for lead (*plumbum*), Hg for mercury (*hydrargyrum*), K for potassium (*kalium*), Ag for silver (*argentum*), Na for sodium (*natrium*), Sn for tin (*stannum*). W is the symbol for tungsten, an element which occurs in the mineral wolfram, and which is called on the continent by the name of this mineral.

The symbols must not be regarded as mere shorthand signs, intended only to save time in representing the names of the elements. They serve not only this purpose, but something more besides. Symbols are employed by chemists with two different significations. In the first of these significations a symbol represents *an atom* of the element for which it is the symbol; in the second it represents *a definite quantity* in grams of that element. These two significations are necessarily distinct, because we do not know the actual weight of any atom. It has been found convenient to arrange that the number of grams of an element represented by its symbol shall be the same as the number which expresses the relative atomic weight of the element. Hence while the symbol C stands for the element carbon, it represents not only one atom of carbon (with the relative atomic weight 12), but also 12 grams of this element. Similarly in the cases of the following symbols: H stands for one atom and for 1 gram of hydrogen; O for one atom and for 16 grams of oxygen; Pb for one atom and for 207 grams of lead, and so on. The symbols for the

elements, with the quantitative value attached to each symbol, are given in the list of atomic weights on p. ii.

Compound substances contain atoms of at least two different elements. In order to represent by means of symbols the composition of the most simply constituted compound, as for example carbonic oxide, a molecule of which, we have seen, is supposed to consist of two atoms—one of carbon and one of oxygen—we must employ two symbols. These symbols are written side by side thus : CO, and constitute a **formula.** When it is necessary to represent more than one atom of the same element in the formula for a compound, the symbol need not be repeated ; but a small figure is written after, and on a somewhat lower level than, the symbol, to indicate how many atoms of the element are to be represented. Thus the formula for carbonic anhydride is usually written CO_2 (not COO), and this indicates that a molecule of the compound is supposed to contain one atom of carbon and two atoms of oxygen (p. 44). In an exactly analogous manner the *formula* for hydrogen gas is written H_2 in order to express the view that hydrogen molecules each consist of two hydrogen atoms (pp. 90, 91).

The beginner must bear in mind that chemical formulæ are based upon, and give short expression to, a number of observed facts concerning the substances which they represent, and that therefore when he knows the formula for a substance he has these facts either immediately before him or within easy reach. We must here make a somewhat long digression, leaving the further description of how chemical notation is employed, in order to study the full significance of the formulæ already given for carbonic oxide and for carbonic anhydride, and, subsequently, to see how we ascertain what formula is to be written to represent each substance. We shall consider first the information which the formulæ CO and CO_2 convey.

(1) The foregoing formulæ show at a glance the

elements and the number of atoms of each, which go to make up the molecules of the gases which they represent. For the purpose of getting this information from them the symbols which constitute these formulæ need only be regarded as possessing their first signification, already referred to (p. 108).

(2) From the formulæ we can easily obtain the relative molecular weights of the two gases, since these are simply the sums of the atomic weights of the atoms represented by the formulæ as existing in the molecules. We obtain them thus—

C = 12	C = 12
O = 16	O_2 = 32 (= 16 × 2)
CO = 28	CO_2 = 44

The relative molecular weight of carbonic oxide, as calculated from its formula, is thus 28, and that of carbonic anhydride is 44.

(3) When the symbols are considered as representing definite weights in grams of the respective elements, as explained already (p. 108), then the formula CO represents 28 grams of carbonic oxide, and CO_2 represents 44 grams of carbonic anhydride, while H_2 represents 2 grams of hydrogen. These quantities are called the **gram molecules**, or the molecular weights in grams, of the respective gases.

(4) The figures given in paragraph 2, above, show the quantitative composition of each of the oxides, since from them we see that 28 grams of carbonic oxide consist of 12 grams of carbon and 16 grams of oxygen, and that 44 grams of carbonic anhydride consist of 12 grams of carbon and 32 grams of oxygen. Should the *composition per cent* of the oxides be required, it can easily be calculated thus—

28 grams of carbonic oxide contain 12 grams of carbon,

$\therefore$ 100 ,, ,, ,, ,, $\frac{12 \times 100}{28} = 42{\cdot}86$ grams C.

28 grams of carbonic oxide contain 16 grams of oxygen,

$\therefore$ 100 ,, ,, ,, ,, $\frac{16 \times 100}{28} = 57{\cdot}14$ grams O.

44 grams of carbonic anhydride contain 12 grams of carbon,

$\therefore$ 100 ,, ,, ,, ,, $\frac{12 \times 100}{44} = 27{\cdot}27$ grams C.

44 grams of carbonic anhydride contain 32 grams of oxygen,

$\therefore$ 100 ,, ,, ,, ,, $\frac{32 \times 100}{44} = 72{\cdot}73$ grams O.

Tabulated results of these calculations are given on p. 42. The composition per cent of any other compound can be calculated from its formula in an analogous manner.

(5) The formulæ CO, CO_2, and H_2 represent the kind and the number of atoms contained in a molecule each of carbonic oxide, carbonic anhydride, and hydrogen, and they are called the **molecular formulæ** for these substances. We have already seen that the relative molecular weights of the same substances are 28, 44, and 2 respectively. The quantities in grams (the gram molecules) represented by these formulæ therefore occupy, in accordance with Avogadro's law, the same volume if measured under the same conditions of pressure and of temperature. The same is true of the gram molecules, or quantities represented by the molecular formulæ, of all other gases. The volume occupied by the gram molecule of any gas is called the **gram molecule volume**, and when numerical expression is given to this volume the pressure and the temperature must also be stated. The gram molecule volume at standard pressure and temperature (760 mm. and 0°) is 22·33 litres, and therefore under these conditions 2 grams of hydrogen, 28 grams of carbonic oxide, 44 grams of carbonic anhydride, and the molecular weights in grams (gram molecules) of other gases occupy 22·33 litres. The gram molecule volume at any other pressure (p) and temperature (t) is—

$$22{\cdot}33 \times \frac{760}{p} \times \frac{273+t}{273} \text{ litres (Chapter VIII.)}$$

From the molecular formula for a gas we can accordingly find at once (by adding up the molecular weight) the weight in grams of the gas which, at 760 mm. and 0°, occupies 22·33 litres. By making simple calculations we can further find what the volume of this quantity would be at any other pressure and temperature, and also what the volume of any other quantity would be either at standard or at any other pressure and temperature. Therefore from the molecular formula for a gas we can find what volume any quantity of the gas would occupy at a given pressure and temperature.

Shortly stated, the information concerning a gas which is embodied in its molecular formula is as follows—

(1) The qualitative composition. (Results of qualitative analysis.)

(2) The quantitative composition. (Results of quantitative analysis.)

(3) The volume occupied by a known weight; or the weight of a known volume of the gas. (Result of relative density determination.)

It is in fact from the experimental determinations of the quantitative composition and of the relative density of a gas, that its formula is deduced.

From the quantitative composition alone, of a compound, its **empirical formula** can be deduced. An empirical formula does not in any respect differ, *in the way in which it is written*, from a molecular formula; but while a molecular formula is designed to express the *actual* number of atoms of each element present in a molecule of the compound represented, an empirical formula only indicates, in the smallest whole numbers, the *relative* numbers of each kind of atoms present in any given weight of the compound represented. The real difference between the two kinds of formulæ can best be made clear by means of an example; and, since the first step towards assigning a molecular formula to

a compound consists in deducing its empirical formula from its composition per cent as obtained from quantitative analysis, we must see how this is done.

The mean results of two analyses of a certain compound of carbon and hydrogen indicated that 100 parts by weight of it contain—

Carbon	85·64[1]
Hydrogen	14·36

It is required to find the relative numbers of carbon and of hydrogen atoms present in the compound. To find this we must ascertain how often the atomic weight of carbon (12) is contained in 85·64, and how often the atomic weight of hydrogen (1) is contained in 14·36. This information is obtained as below—

$$\text{(Carbon)}\ \frac{85{\cdot}64}{12} = 7{\cdot}14,$$

$$\text{(Hydrogen)}\ \frac{14{\cdot}36}{1} = 14{\cdot}36.$$

The resulting numbers exhibit the required relation of the numbers of atoms, but not expressed in the simplest ratio in whole numbers. To find the latter, both results must be divided by the smaller of the two, thus—

$$\text{(Carbon)}\ \frac{7{\cdot}14}{7{\cdot}14} = 1,$$

$$\text{(Hydrogen)}\ \frac{14{\cdot}36}{7{\cdot}14} = 2{\cdot}01,$$

when it is seen that the ratio, as experimentally determined, is practically as 1 to 2. From this we conclude that the compound contains two hydrogen atoms for every carbon atom. This relation is expressed by the

[1] The separate results were: carbon 85·65 and 85·64, hydrogen 14·26 and 14·46.

empirical formula CH_2, and we cannot get any more information from the composition per cent alone. The next question that arises is, whether the formula CH_2 is also the *molecular formula* for the compound. If it is, the molecular weight of the substance, as calculated from the formula (p. 110), is 14 ($C = 12$ and $H_2 = 1 \times 2$), and the relative density corresponding to this molecular weight is 7. The substance under examination is a liquid, and when its vapour density (the relative density of its vapour) was determined (p. 86) it was found to be 81·4. The molecular weight is therefore $81{\cdot}4 \times 2 = 162{\cdot}8$ (p. 92), and nearly twelve times that which corresponds to the formula CH_2. This points to twelve times CH_2 as representing the molecular formula, and the latter is accordingly written $C_{12}H_{24}$.

The student should note that the results of one or two analyses of a compound usually indicate a composition per cent which differs slightly from that calculated from the formula (or from the theoretical numbers, as the calculated composition per cent is commonly called), and that therefore the numbers obtained as above, indicating the simplest ratio of the atoms in a compound, are seldom obtained as *exactly* whole numbers. In the case just mentioned the mean results of the two analyses lead to the ratio of carbon atoms to hydrogen atoms of 1 to 2·01. This observed irregularity indicates slight errors in the quantitative analyses, and the more accurately the analyses are made, the smaller will such irregularity become.

In a great many cases the empirical formula for a compound is also the molecular formula, the molecular weight of the compound corresponding to the arithmetically simplest formula which represents the composition per cent—that is to the empirical formula. The quantity denoted by the empirical formula for a substance to which a molecular formula cannot be assigned (p. 115) is called the **formula weight** of the substance.

The student should note particularly that the quantitative composition of a substance leads to the empirical formula only, and that a molecular formula can only be assigned when the molecular weight is known. Since the molecular weights of gases can be obtained from their relative densities (p. 92) by multiplying the numbers representing the latter by 2, molecular formulæ can be assigned to all these substances. Further, since vapour densities of those substances which are solid or liquid at ordinary temperatures, but can be obtained in the gaseous state without undergoing decomposition when their temperature is sufficiently raised, are exactly analogous to the relative densities of gases and similarly lead to their molecular weights when in the gaseous state, molecular formulæ can be written to represent the molecules of these substances when they exist in the gaseous state. Thus the formula H_2O represents the composition of the molecules which exist in water vapour. We are not justified, however, in assuming that the formula which represents a molecule of a substance in the gaseous state also represents a molecule of it when in the liquid or solid state; and the evidence points to the contrary in some cases, where two or more gaseous molecules very probably unite to form one molecule of the liquid or solid (compare Chapter XV.). Besides vapour density determinations, there are several other methods by which molecular weights may be estimated, and these are therefore of importance in assigning formulæ to some substances. A number of these methods are mentioned in Chapter XVI.

There are numerous compounds to which the methods of molecular weight determination at present known are not applicable, and the molecular weights of these compounds are consequently unknown. In giving formulæ to these substances the quantitative composition is alone available, and hence only an empirical formula can be given. This is what is done, for example, in the cases

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of various metallic oxides which cannot be obtained as gases, such as the oxides of iron, zinc, magnesium, calcium, gold, etc., and in all other cases where the molecular weight cannot be ascertained.

As has been said already, empirical and molecular formulæ are written in the same way, and the student must learn in each case where the arithmetically simplest formula occurs, whether this is a molecular formula or not. When formulæ are employed which are not the arithmetically simplest, he may conclude that these are molecular formulæ.

Such formulæ as $Ba(NO_3)_2$ (for barium nitrate) and $Fe_2(SO_4)_3$ (for ferric sulphate) are often written. In these cases the small figure placed outside the brackets refers to and multiplies all that is enclosed within the brackets. A figure placed in front of a formula multiplies the whole formula. For example $2Ba(NO_3)_2$ and $3Fe_2(SO_4)_3$ represent respectively twice as much barium nitrate and three times as much ferric sulphate as the simple formulæ themselves represent. Two or more formulæ are sometimes written side by side, but separated by a comma ; as $CuSO_4,5H_2O$. This formula represents the composition of crystallised cupric sulphate, as if this substance were composed of one molecule of cupric sulphate associated with five molecules of water.

Chemical formulæ are employed in writing **chemical equations.** These are intended to represent the chemical changes which occur during chemical actions, and they convey a great deal of information respecting these actions. In writing a chemical equation, formulæ representing the quantity of each substance which enters into the action are placed on one side, and formulæ representing the quantity of each product are placed on the other side of the sign of equality (=). Between the various formulæ on each side signs of addition (+) are placed. These signs are not used in the same sense as in a mathematical equation ; and a chemical equation

so-called, is, in fact, only an equation in so far that all the materials represented on the one side must be accounted for in some form on the other side. Chemical equations are, as a rule, only true as a record of facts when read in one direction (namely from left to right), since most chemical reactions are not capable of being directly reversed.

The chemical change which occurs when zinc is placed in dilute sulphuric acid is represented by the equation—

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

This equation may be read: zinc and sulphuric acid produce hydrogen and zinc sulphate. In addition to this qualitative meaning, however, it also expresses the quantitative relations between the substances concerned, for each symbol and formula has its own quantitative signification. It may therefore be read; 65 grams of zinc and 98 grams of sulphuric acid produce 2 grams of hydrogen and 161 grams of zinc sulphate. If we require the volume of the quantity of hydrogen represented, instead of its weight, we may say that 65 grams of zinc and 98 grams of sulphuric acid produce a quantity of hydrogen which at 0° and 760 mm. occupies 22·33 litres, and also 161 grams of zinc sulphate. When we thus know how much zinc and sulphuric acid are required to produce 2 grams or (at 0° and 760 mm.) 22·33 litres of hydrogen, we can calculate how much of each would be required to produce any other weight of the gas; or any other volume, either under the same or under different conditions of temperature and of pressure. Chemical equations therefore indicate the proportions in which the reacting substances act upon each other, and they show also how much of each product (and the volume if gaseous) can be obtained from known quantities of materials, as the result of the actions which they represent.

The beginner should exercise himself not only in the interpretation, as above, of the full meaning of printed equations as he finds them in text-books, but also in the working out of numerous quantitative problems based upon such equations. The following variations of the same problem may serve as examples of such calculations—

(1) What quantity of oxygen in grams can be obtained from 450 grams of mercuric oxide?

The equation representing the chemical change that occurs when mercuric oxide is heated is—

$$2HgO = 2Hg + O_2,$$

and from it we learn that 432 ($=2\times216$) grams of mercuric oxide yield 32 ($=2\times16$) grams of oxygen. The quantity of oxygen obtainable from 450 grams of mercuric oxide is therefore $\frac{450\times32}{432} = 33{\cdot}33$ grams.

(2) What volume of oxygen in litres measured at 0° and 760 mm. can be obtained from 450 grams of mercuric oxide?

The equation already given shows that 432 grams of mercuric oxide yield 22·33 litres of oxygen at 0° and 760 mm. 450 grams therefore yield $\frac{450\times22{\cdot}33}{432} = 23{\cdot}26$ litres at 0° and 760 mm.

(3) What volume of oxygen in litres measured at 36° and 1000 mm. can be obtained from 450 grams of mercuric oxide?

This example differs from the last only in the temperature and the pressure under which the oxygen is measured. It is only necessary to substitute for 22·33 litres in the last example the volume which 22·33 litres become at the new temperature and pressure, that is $\left(22{\cdot}33\times\frac{760}{1000}\times\frac{273+36}{273}\right)$. The volume of oxygen obtainable from 450 grams of mercuric oxide measured under these conditions is therefore $\frac{450\times\left(22{\cdot}33\times\frac{760}{1000}\times\frac{309}{273}\right)}{432} = 20$ litres, at 36° and 1000 mm.

In constructing equations it is always necessary, and it is usually sufficient, to know the formulæ for the substances which enter into the action, and the formulæ for the products. Suppose that an equation is to be constructed to represent the change which occurs when dilute hydrochloric acid acts upon calcium carbonate.

The formula for calcium carbonate is $CaCO_3$, and that for hydrochloric acid is HCl. In the reaction, the whole of the carbon which the calcium carbonate contains is liberated as carbonic anhydride (formula CO_2); and calcium chloride (formula $CaCl_2$) and water (formula H_2O) are the other products. The equation may therefore be written in a preliminary manner as follows—

$$CaCO_3 + HCl = CaCl_2 + CO_2 + H_2O.$$

But an inspection of this equation shows that it is erroneous, because there are two atoms of hydrogen and two of chlorine represented after the sign of equality, while there is only one atom of each represented before it. This plainly indicates (since the formulæ are all correctly written) that the quantity of hydrochloric acid represented by HCl is not sufficient to act upon the whole quantity of calcium carbonate represented by the formula $CaCO_3$. The deficiency is just equal to the quantity represented by the formula HCl, and the equation can only be written correctly by introducing $2HCl$ instead of HCl, thus—

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

The equation may then be read: 100 grams of calcium carbonate are acted upon by 73 grams of hydrochloric acid; and 111 grams of calcium chloride, 44 grams (or 22·33 litres at 0° and 760 mm.) of carbonic anhydride and 18 grams of water are the products. If 100 grams of calcium carbonate were in an actual experiment treated with 36·5 grams of hydrochloric acid (as indicated by the preliminary incorrect equation) one half of it would simply remain over unacted upon, while only half of the quantities mentioned above of the various products would be obtained.

We shall now examine an equation representing a case in which only gases enter into chemical action,

and in which the product is also a gas, in order to show that, apart altogether from the weights of the gases concerned, such equations indicate the relative volumes of the gases entering into and resulting from chemical actions. The equation representing the change which takes place when carbonic oxide burns in air or oxygen is the following—

$$2CO + O_2 = 2CO_2.$$

But the formulæ CO, O_2, and CO_2, being the molecular formulæ for the gases which they represent, all represent, at the same temperature and pressure, equal volumes of these gases (p. 111); hence, taking volumes alone into account, 2CO represents double the volume that O_2 represents, and the same volume that $2CO_2$ represents. The equation accordingly expresses the fact that any given volume of carbonic oxide combines with half its volume of oxygen, and that the volume of carbonic anhydride produced is the same as that of the carbonic oxide burned.

The beginner should construct equations for himself to represent chemical actions. He is recommended to do so for all the cases of combination and decomposition mentioned in the tables on pp. 48 and 49, and for some other simple reactions; and then to proceed to more complicated reactions. All such equations should be submitted to a teacher, in order that any errors may be pointed out and rectified.

CHAPTER XIII

BASES—ACIDS—SALTS

Bases and **acids** form two highly important classes of chemical compounds. The members of each class are entirely different from those of the other class in their general chemical characters. Bases usually enter into chemical reaction with acids with great readiness, and in so doing they give rise to a third most important class of compounds which are called **salts**. It is the main purpose of this chapter to give a general account of the chemical nature and characters of bases and of acids, and to show the relation of both these classes of substances to salts. We shall, however, defer the study of the most important chemical properties of bases and of acids until we have inquired into the kinds of substances which are comprised in these groups.

We have already seen in Chapter VII. (p. 60) that almost every element forms one or more compounds with oxygen, and that the oxides so formed may be divided into three groups. These groups are—

(1) Basic oxides.

(2) Acid oxides or acid anhydrides.

(3) Oxides which are neither basic oxides nor acid oxides.

The oxides belonging to group 1 are all derived from the metallic elements. Every metal forms at least one such basic oxide, while several form more than one.

The oxides belonging to group 2 are mostly derived from the non-metallic elements; but a few metals, besides forming one or more basic oxides, also give rise to oxides which are acid anhydrides. Some of the oxides belonging to group 3 are derived from metallic and some from non-metallic elements. We are only incidentally concerned in the present chapter with the oxides belonging to this group.

A number of basic oxides combine readily with water to form basic hydrates or hydroxides. Calcium oxide (quicklime), for example, combines with water to form calcium hydroxide (slaked lime), as illustrated by the equation :—

$$CaO + H_2O = Ca(HO)_2.$$ (See Experiment 13.)

The basic oxides and hydroxides of the metals form one of the largest classes of bases.

The acid oxides or acid anhydrides combine with water to form acids. The name anhydride is often given to the substance which remains when the elements of water are removed from a compound. Many acids yield acid anhydrides when the elements of water are thus removed from them; and, as stated above, the acid anhydrides often combine with water to form acids. Thus, for example, sulphuric anhydride combines with water to form sulphuric acid, as illustrated by the equation—

$$SO_3 + H_2O = H_2SO_4.$$

One of the most important classes of acids is derived in this way from the acid anhydrides.

In addition to those bases and acids which may be regarded as derived from certain of the oxides of the elements, there are a large number of other bases and acids which cannot be so regarded, and many of which do not even contain any oxygen. Examples of such bases are furnished by ammonia NH_3, by the substituted

ammonias, such as methylamine, NH_2CH_3, dimethylamine, $NH(CH_3)_2$, and trimethylamine, $N(CH_3)_3$; and by numerous other more or less complicated compounds of nitrogen, of phosphorus, or of other elements, some of which compounds do and some of which do not contain oxygen also. Examples of acids which cannot be regarded as derived from the oxides of the elements are furnished by the halogen acids (hydrofluoric, HF; hydrochloric, HCl; hydrobromic, HBr; hydriodic, HI) and by hydrocyanic acid, HCN, none of which contain oxygen; and further by the very large class of organic acids containing oxygen, of which acetic, oxalic, tartaric, citric, and benzoic acids may be mentioned as examples.

Oxygen was at one time regarded as a necessary constituent of all acids, and its name (derived from Greek words signifying "acid producer") was given to it by Lavoisier in consequence of this view, which is now known to be erroneous.

Bases and acids are not all soluble in water, but solutions of those which do dissolve produce in certain colouring matters changes of colour which indicate respectively an "*alkaline*" (or basic) and an "*acid*" reaction. The reaction of a solution of a base is called the alkaline reaction, because this is the reaction produced by solutions of the "alkalies" caustic potash and caustic soda (potassium hydroxide and sodium hydroxide), which are strong bases.

Experiment 28.—Procure some red and some blue litmus papers, and some yellow turmeric paper. Dip narrow strips of each kind into dilute solutions of caustic potash and of sulphuric acid. Observe that the red litmus is turned blue, and the yellow turmeric turned brown by the solution of caustic potash, while the blue litmus remains unaltered; also that the blue litmus is turned red by the solution of sulphuric acid while the red litmus and the yellow turmeric remain unaltered.

Solutions of strong bases generally possess a peculiar

and characteristic soapy taste, which may be observed by tasting a few drops of lime-water or of a *highly diluted* solution of caustic potash. Solutions of acids possess a characteristic sour taste. This may be observed by tasting vinegar (which contains acetic acid) or almost any unripe fruit. Tartaric acid is present in unripe grapes; citric acid is present in lemon juice; malic acid is the acid present in many of the unripe fruits of temperate climates, as, for example, in apples, gooseberries, etc.

Bases and acids stand in a very important relation to each other, since they enter in most cases into chemical interaction, and in doing so produce salts. The formation of salts in this way may or may not be accompanied by the simultaneous formation of water. The following examples will illustrate the formation of salts by this method. When quicklime is treated with hydrochloric acid, or sulphuric acid, or nitric acid, a salt—calcium chloride, or sulphate, or nitrate—is formed, and water is formed simultaneously, thus—

$$CaO + 2HCl = CaCl_2 + H_2O.$$
$$CaO + H_2SO_4 = CaSO_4 + H_2O.$$
$$CaO + 2HNO_3 = Ca(NO_3)_2 + H_2O$$

Exactly analogous to these cases are those of the action of the same acids upon slaked lime (calcium hydroxide) a salt being formed as before. In these cases, however, more water is produced. For example—

$$Ca(HO)_2 + 2HCl = CaCl_2 + 2H_2O.$$

In some cases a basic oxide and an acid anhydride combine directly to form a salt, without the simultaneous formation of water. For example, quicklime and carbonic anhydride combine to form calcium carbonate, thus—

$$CaO + CO_2 = CaCO_3.$$

When ammonia and hydrochloric acid gases are

mixed in equal proportions by volume, a salt—ammonium chloride—is formed as the only product of the action—

$$NH_3 + HCl = NH_4Cl.$$ (See Experiment 9.)

In all the actions mentioned in the preceding examples, the bases and acids concerned entirely lose their basic and acid characters respectively and give rise to products (a salt and water, or only a salt) which have no effect upon test papers (litmus, turmeric, etc.), and are therefore said to be *neutral.* The solutions of a great many salts are neutral; but the name salt is also applied to numerous substances which resemble these neutral salts in many respects, although they yield solutions which are alkaline or acid to test papers (see p. 123).

Experiment 29.—Take a solution of potassium hydroxide (caustic potash) and carefully add to it a solution of hydrochloric acid until the mixed solution is found, by means of litmus paper, to be neutral. (Write an equation representing the change which occurs.) Then evaporate the solution to dryness in a porcelain basin. Observe that a white solid substance remains behind. This white solid is a neutral salt. It is named potassium chloride. Dissolve it in water and observe the taste of the solution.

We have seen (p. 124) that when calcium oxide is acted upon by the necessary quantity of hydrochloric acid, the whole of the oxygen which it contains unites with the hydrogen of the acid to form water, while the chlorine of the acid takes the place of this oxygen, and a salt—calcium chloride—is produced. The change which occurs when we employ nitric, sulphuric, or other acid containing oxygen, instead of hydrochloric acid, is exactly analogous; but in such a case the oxygen of the oxide is replaced, not by the single atom chlorine, but by a more or less complex group of atoms. An oxide of a metal is said to be a *basic* oxide when by the

action upon it of acids we can obtain from it a series of *corresponding* salts. The chloride which thus "corresponds" to any basic oxide contains two atoms of chlorine for each oxygen atom of the oxide. The corresponding nitrate contains two (NO_3) groups, and the corresponding sulphate contains one (SO_4) group instead of each oxygen atom of the basic oxide. Such groups of atoms as those just mentioned are called by the general name *radicals*. In the case of salts, that part of the salt which is not metal is called the *salt-radical*.

The following table shows the composition of some of the salts corresponding to a number of basic oxides, and also illustrates the fact that the substances produced by the action of acids upon other basic oxides are analogous in composition to those produced by their action on calcium oxide.

Basic Oxide.	Corresponding Chloride.	Corresponding Nitrate.	Corresponding Sulphate.
K_2O	(2)KCl	(2)KNO_3	K_2SO_4
CaO	$CaCl_2$	$Ca(NO_3)_2$	$CaSO_4$
FeO	$FeCl_2$	$Fe(NO_3)_2$	$FeSO_4$
Fe_2O_3	(2)$FeCl_3$	(2)$Fe(NO_3)_3$	$Fe_2(SO_4)_3$

In the cases of potassium chloride and nitrate, and of ferric chloride and nitrate, the quantity of each of these produced from the quantity of basic oxide represented, is twice that represented by the formulæ for these salts as given above.

Since the oxygen of the basic oxide has, in each of the cases given in the table, combined with the hydrogen of the acid (hydrochloric, nitric, or sulphuric) to form water, we may regard the salt produced as being formed either by a part of the acid (Cl, NO_3, SO_4) taking the

place of the oxygen of the oxide, or by the metal of the oxide taking the place of the hydrogen of the acid; and in this way we come to look upon a salt so produced as being made up of two parts—the *metal* which is obtained from the basic oxide, and the *salt radical* which is obtained from the acid. We shall see that all salts may be regarded in the same way as composed of metal (or that which plays the part of metal as, for example, the radical NH_4, which is assumed to exist in all the ammonium salts) and of salt radical. The salt radical of a salt may be a single atom, such as chlorine or bromine, or it may be a *compound radical*, such as NO_3 or SO_4. For further discussion of salts from this point of view, see in the chapter on Electrolysis (p. 184).

There is one important characteristic of acids in which they all agree. All acids contain hydrogen, which is, as we have already seen, capable of having its place taken by metals with the formation of salts. When hydrochloric acid is neutralised by the addition of caustic potash (cf. Experiment 29), potassium chloride is formed—

$$HCl + KOH = KCl + H_2O.$$

A molecule of nitric acid or of hydrochloric acid contains only one atom of hydrogen, and in potassium nitrate or chloride the place of this hydrogen atom is taken by an atom of potassium. It is not possible to suppose that the hydrogen of nitric acid or of hydrochloric acid can therefore be displaced by potassium in more than one stage; if any hydrogen is displaced from the molecule it must all be displaced. In the case of sulphuric acid, H_2SO_4, or of oxalic acid, $H_2C_2O_4$, the molecule contains two hydrogen atoms. The place of the whole of the hydrogen in either of these acids may be taken by potassium when the acid is treated with caustic potash. In either case the hydrogen may be displaced in two successive stages. One atom of potassium first takes

the place of one atom of hydrogen, yielding the compound $KHSO_4$ (or KHC_2O_4), thus—

$$H_2SO_4 + KOH = KHSO_4 + H_2O,$$

and then a second potassium atom takes the place of the second hydrogen atom, yielding K_2SO_4 (or $K_2C_2O_4$), thus—

$$KHSO_4 + KOH = K_2SO_4 + H_2O.^1$$

The quantity of caustic potash which is required to displace all the hydrogen contained in a molecule of sulphuric or of oxalic acid is thus twice the quantity required to displace that contained in a molecule of nitric acid or of hydrochloric acid. This capacity of the molecules of different acids for entering into reaction with different quantities of one and the same base is called the *basicity* of the acids, and acids are said to be *monobasic*, *dibasic*, *tribasic*, etc., according to whether their molecules possess the same basicity as nitric and hydrochloric acids, or double, treble, etc., this basicity. Nitric and hydrochloric acids are monobasic; sulphuric and oxalic acids are dibasic; orthophosphoric and citric acids are tribasic, and so on.

In an exactly analogous way bases differ in their *acidity*, or capacity for entering into reaction with one and the same acid. Taking, for example, the hydroxides of potassium, of calcium, and of bismuth, the quantities represented by the formulæ KHO, $Ca(HO)_2$, and $Bi(HO)_3$ are capable of reacting respectively with one, two, and three times the quantity of nitric or of hydrochloric acid represented by the formula HNO_3 or HCl, thus—

$$KHO + HNO_3 = KNO_3 + H_2O.$$
$$Ca(HO)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O.$$
$$Bi(HO)_3 + 3HNO_3 = Bi(NO_3)_3 + 3H_2O.$$

[1] The fact that the hydrogen of sulphuric acid and of oxalic can thus be displaced in two successive stages is evidence that these acids contain two hydrogen atoms in their molecules.

These three bases are said to be *monacid*, *diacid*, and *triacid* respectively.

The quantity of a diacid base which is represented by its formula reacts with the quantity of a dibasic acid represented by the formula for the latter, thus—

$$Ca(HO)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$$

When the whole of the displaceable hydrogen of an acid has its place taken by a metal, the substance which is produced is called a *normal salt.* Normal salts are frequently neutral also, that is, solutions of many of them do not possess either an acid or an alkaline reaction ; but normal salts yield in many cases solutions which are not neutral, some possessing an acid and some an alkaline reaction. Thus sodium carbonate, Na_2CO_3, yields a strongly alkaline solution, while the solution of cupric sulphate, $CuSO_4$, is distinctly acid.

When only a part of the displaceable hydrogen of a dibasic acid or acid of greater basicity is displaced by a metal, the substance which is produced is intermediate in composition between the acid and the normal salt, and is called an *acid salt.* Thus the substances represented by the formulæ $KHSO_4$ and KHC_2O_4 are acid salts. The names given to these substances are—

$KHSO_4$.	KHC_2O_4.
Acid potassium sulphate.	Acid potassium oxalate.
Potassium hydrogen sulphate.	Potassium hydrogen oxalate.
Potassium bisulphate.	Potassium binoxalate.

The last names given above are old ones, and they indicate that the substances contain twice as much of the salt radical in proportion to the potassium as the corresponding normal salt contains.

It is important to note in connection with these so-called acid salts that they are thus named because they possess the chemical character of acids, in so far that they contain hydrogen which may have its place taken by a

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metal, *and not because of the reaction of their solutions to test papers.* The behaviour towards test papers of the solutions of acid salts may indicate an acid reaction, or neutrality, or even an alkaline reaction. The word "acid" is thus used as an adjective with two entirely different significations, and the student must therefore distinguish carefully between acid *character* and acid *reaction.*

Just as there are acid salts which are intermediate in composition between the acid and the normal salt, so there are in many instances compounds intermediate in composition between the normal salt and the base. These are called *basic salts*, because they possess the chemical character of bases in so far that they interact with acids to form normal salts. Oxychloride of bismuth, BiOCl, is such a basic salt. When it is treated with hydrochloric acid the normal chloride is formed thus—

$$BiOCl + 2HCl = BiCl_3 + H_2O.$$

That this basic salt is intermediate in composition between the basic oxide, Bi_2O_3, and the corresponding chloride, $BiCl_3$, may be clearly seen by observing that $3BiOCl$ represents the same number of bismuth, oxygen, and chlorine atoms as $(Bi_2O_3 + BiCl_3)$. The substance represented by the formula $Cu_3(OH)_4SO_4$ is similarly a basic salt, being intermediate in composition between cupric sulphate, $CuSO_4$, and cupric hydrate, $Cu(OH)_2$. In the formula $Cu_3(OH)_4SO_4$ the same kinds of atoms and the same number of each are represented as in $(CuSO_4 + 2Cu(OH)_2)$.

Salts are formed in other ways besides by the mutual interaction of bases and acids. Some of these ways are very important, and are frequently made use of. When a metal dissolves in an acid, a salt is almost always produced. Iron, for example, dissolves in dilute sulphuric acid, yielding hydrogen and a salt, ferrous sulphate—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Copper does not dissolve in dilute sulphuric acid, but sulphuric acid, when strong and hot, dissolves it. A salt—cupric sulphate—is formed under these circumstances, but instead of hydrogen being given off, substances are obtained—sulphurous anhydride and water—which may be regarded as being produced by the reducing action of hydrogen upon hot sulphuric acid—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

In some special cases this method of preparing salts is the only one employed on the manufacturing scale. Thus silver nitrate is prepared by dissolving silver in nitric acid, and then evaporating the solution in order that the salt may crystallise out. During the solution of the metal, nitric oxide is given off—

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O.$$

In many instances the metal of a salt may be displaced from its combination by the action of another metal, the other metal forming a new salt by combining with the salt radical of the original salt. For example, when strips of iron are introduced into a solution of cupric sulphate, a deposit of copper is produced upon the surface of the iron, while some of the iron goes into solution in the form of ferrous sulphate—

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

Again, when a solution of silver nitrate is poured into a glass vessel, and a small cloth bag containing a little mercury is suspended in the solution, crystals of metallic silver are slowly formed on the outside of the bag, and some of the mercury goes into solution as mercurous nitrate—

$$AgNO_3 + Hg = HgNO_3 + Ag.$$

Experiment 30.—Dip a clean steel knife blade into a solution of cupric sulphate and keep it there for a few seconds. Then withdraw it and observe that the part which the solution has touched has had a red deposit of metallic copper formed upon it.

Experiment 31.—Vary Experiment 30 by adding a quantity of clean iron filings or turnings to some cupric sulphate solution contained in a bottle. Cork the bottle and shake it up with its contents from time to time during several hours. Observe that the copper is rapidly precipitated, and that the blue colour of the solution becomes thereby less intense. If enough iron is used, and if the experiment is continued for a sufficient length of time, the whole of the copper is eventually precipitated, and the blue colour of the solution entirely disappears.

Experiment 32.—Prepare a "lead tree" by suspending some strips of zinc for a few hours in a solution of lead nitrate. Observe the colour and crystalline character of the lead which is precipitated. Zinc nitrate is formed in solution. Write an equation representing the action. What weight of zinc will displace 5 grams of lead from solution? [Answer, 1·57 gram.]

Further methods by which new salts are obtained from substances which are frequently salts themselves, will be mentioned in Chapters XIX. and XX.

We have just seen how iron may displace copper from its combination in cupric sulphate, forming ferrous sulphate, while copper is deposited in the state of metal. The change which occurs when iron acts upon dilute sulphuric acid, forming ferrous sulphate, while hydrogen is liberated and escapes as gas, may be regarded as exactly analogous to this. The equations representing both of these changes are given again below for the purpose of comparison—

$$CuSO_4 + Fe = FeSO_4 + Cu.$$
$$H_2SO_4 + Fe = FeSO_4 + H_2.$$

Acids in this and in some other important respects (see for example in Chapter XVII.) closely resemble salts, and are hence sometimes called hydrogen salts. Thus sulphuric acid and hydrochloric acid are frequently called hydrogen sulphate and hydrogen chloride respectively, being regarded as the hydrogen terms in the series of sulphates and of chlorides. Other acids are designated in an analogous manner as hydrogen salts. In the acids, or hydrogen salts, hydrogen is regarded as playing the part of the metal of the salt. Hence hydrogen may be said to possess some of the chemical characters of a metal.

Pairs of salts in some instances combine with each other to form *double salts*. There are some very important series of such double salts. Of these series one of the best known includes the salts called *alums*. Common ammonia alum is a double aluminium and ammonium sulphate, and it contains also water of crystallisation. It is made by mixing, in proper proportions, solutions of aluminium sulphate, $Al_2(SO_4)_3$, and of ammonium sulphate, $(NH_4)_2SO_4$, and evaporating down the solution. The composition of the salt obtained is represented by the formula $Al_2(NH_4)_2(SO_4)_4,24H_2O$. Other alums can be prepared which contain sodium, potassium, cæsium, or other metal in place of the ammonium; and the name "alum" is further extended to include double salts which do not contain aluminium at all, but contain iron, chromium, or other metal in place of the aluminium of common alum. "Chrome alum," for example, has the composition represented by the formula $Cr_2K_2(SO_4)_4,24H_2O$. The alums all crystallise in the same crystalline form.

Rochelle salt is a double salt, and is intermediate in composition between potassium tartrate, $K_2C_4H_4O_6$, and sodium tartrate, $Na_2C_4H_4O_6$. It is prepared by evaporating down the solution obtained by mixing these two substances, dissolved in water, in the proportions repre-

sented by the above formulæ. The formula representing the composition of the double salt is $KNaC_4H_4O_6$.

Double salts can also be obtained which contain one metal and two salt radicals. For example, mercuric chloriodide, HgClI, contains mercury in combination with both chlorine and iodine. It is formed when mercuric iodide is dissolved in solution of mercuric chloride and the solution is evaporated down.

Certain sulphides of metals and of non-metals exhibit chemical characters closely resembling those of the corresponding oxides with respect to the formation of salts. Thus carbon bisulphide, CS_2, is acted upon by a solution of sodium sulphide, Na_2S, with formation of sodium thiocarbonate, Na_2CS_3, a salt exactly analogous to sodium carbonate, Na_2CO_3, but containing sulphur instead of the oxygen which the latter contains. Other thio-salts are known which are similarly obtained by the interaction of so-called thio-acids and thio-bases.

There are several series of salts known containing salt radicals which do not exist in known acids. For example, the carbonates, the sulphites, and the chromates (such as Na_2CO_3, Na_2SO_3, Na_2CrO_4) may be regarded as the metallic derivatives from the acids H_2CO_3, H_2SO_3, and H_2CrO_4; but these acids themselves cannot be prepared in a state of purity. The corresponding acid anhydrides—CO_2, SO_2, and CrO_3—are all known, and these dissolve in water. It is probable that the aqueous solutions contain some of the respective acids, but the latter are obtainable only in this way in presence of water, from which they cannot be separated without undergoing decomposition. In the cases of some other series of salts, neither the corresponding acids nor the acid anhydrides are known. The manganates furnish an example of such a set of salts. The sodium salt has the composition represented by the formula Na_2MnO_4. The formulæ for the hypothetical acid and acid anhydride are H_2MnO_4 and MnO_3 respectively.

There are a few oxides of elements which do not possess either a basic or an acid character in a strongly marked manner, and yet are capable to a limited extent of playing the part either of a basic oxide or of an acid anhydride. Such oxides behave like feebly basic oxides towards some acids of very well-marked acid character, and like feebly acid anhydrides towards bases possessing a well-marked basic character. Arsenious oxide, As_4O_6, is an example of such an oxide. It dissolves in hydrochloric acid, forming a solution of arsenious chloride, $AsCl_3$—

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$

It also dissolves in solutions of alkalies, as, for example, in solution of potassium hydroxide, forming solutions of arsenites—

$$As_4O_6 + 8KOH = 4K_2HAsO_3 + 2H_2O.$$

It is important to note that in arsenious chloride, arsenic plays the part of the metal of the salt and chlorine that of the salt radical, while in potassium arsenite, potassium is the metal and arsenic forms a part of the salt radical. The beginner should note in connection with the above chemical characters of arsenious oxide, the fact that arsenic is one of the elements on the border line between the metals and the non-metals, possessing to a certain extent the characters of both.

The following table gives (column I.) the names of a number of series of salts, with (column II.) the formulæ of the normal sodium salts and (columns IV. and V.) of the corresponding acids and acid anhydrides, when these are known. The formulæ of the acid salts are also given (column III.).

I. Name of Series of Salts.	II. Normal Salt.	III. Acid Salt or Salts.	IV. Acid (Hydrogen Salt)	V. Acid Anhydride.
Carbonates	Na_2CO_3	$NaHCO_3$	(5) $[H_2CO_3]$	CO_2
Sulphites	Na_2SO_3	$NaHSO_3$	(5) $[H_2SO_3]$	SO_2
Sulphates	Na_2SO_4	$NaHSO_4$	H_2SO_4	SO_3
Hypochlorites	$NaClO$		$HClO$	Cl_2O
Thiosulphates	$Na_2S_2O_3$	(3)	(5) $[H_2S_2O_3]$	
Cyanides	$NaCN$		HCN	
Nitrites	$NaNO_2$		HNO_2	N_2O_3
Nitrates	$NaNO_3$		HNO_3	N_2O_5
Chlorides	$NaCl$		HCl	
Bromides	$NaBr$		HBr	
Iodides	NaI		HI	
Orthophosphates	Na_3PO_4	NaH_2PO_4, Na_2HPO_4	H_3PO_4	P_2O_5
Arsenites	(1) $[Ag_3AsO_3]$	Na_2HAsO_3	(5) $[H_3AsO_3]$	As_4O_6
Arseniates	Na_3AsO_4	NaH_2AsO_4, Na_2HAsO_4	H_3AsO_4	As_2O_5
Oxalates	$Na_2C_2O_4$	$NaHC_2O_4$	$H_2C_2O_4$	
Borates	(2) Na_3BO_3 (?)		H_3BO_3	B_2O_3
Chromates	Na_2CrO_4	(4) $[Na_2Cr_2O_7]$	(5) $[H_2CrO_4]$	CrO_3
Chlorates	$NaClO_3$		$HClO_3$	
Acetates	$NaC_2H_3O_2$		$HC_2H_3O_2$	(6) $(C_2H_3O)_2O$
Manganates	Na_2MnO_4			
Permanganates	$NaMnO_4$		$HMnO_4$	Mn_2O_7
Tartrates	$Na_2C_4H_4O_6$	$NaHC_4H_4O_6$	$H_2C_4H_4O_6$	

(1) Normal sodium arsenite $[Na_3AsO_3]$ does not seem to have been obtained.
(2) The existence of normal sodium borate is somewhat uncertain.
(3) Apparently there is not a sodium hydrogen thiosulphate. (4) See p. 138.

The element chromium forms compounds which illustrate a number of the matters regarding bases, acids, and salts which have already been discussed in this chapter; and the following further illustrations of these matters are all taken from amongst the compounds of this element.

Chromium forms two basic oxides, CrO and Cr_2O_3, and also an acid anhydride, CrO_3. Of the two basic oxides only chromic oxide, Cr_2O_3, is well known. Corresponding to chromic oxide there is the important series of chromic salts. (Chromous oxide CrO and chromous salts are of no practical importance.) In the chromic salts—examples, chromic sulphate, $Cr_2(SO_4)_3$, and chromic chloride, $CrCl_3$—chromium is the metal of the salts. In the chromates, the important set of salts connected with the acid anhydride (chromic anhydride, CrO_3), chromium forms a part of the salt radical. Examples of chromates are, potassium chromate, K_2CrO_4, and lead chromate, $PbCrO_4$. As has already been stated the corresponding acid, chromic acid, is only known in aqueous solution.

When lead chromate (chrome yellow) is boiled with lime-water, one-half of the chromium and part of the oxygen which it contains is removed, calcium chromate and water being produced, besides a basic lead chromate. The change is represented by the equation—

$$2PbCrO_4 + Ca(HO)_2 = CaCrO_4 + H_2O + Pb_2CrO_5.$$

The basic salt is intermediate in composition between lead oxide, PbO, and lead chromate, $PbCrO_4$. Its formula represents the same kinds of atoms and the same number of each as $(PbO + PbCrO_4)$.

When sulphuric acid is added to a solution of potassium chromate, one-half of the potassium and part of the oxygen which the chromate contains is removed, potassium sulphate and water being produced, besides a

new salt which is called potassium bichromate. The change is represented by the equation—

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

Potassium bichromate is sometimes called an acid salt, but since it does not contain any hydrogen it does not fall within the group of acid salts as these have been defined on p. 129. Nevertheless this substance in a sense corresponds to the acid salts of other series, because it is intermediate in composition between the normal salt, K_2CrO_4, and chromic anhydride, CrO_3. Its formula represents the same kind of atoms, and the same number of each as $(K_2CrO_4 + CrO_3)$. Further, potassium bichromate in aqueous solution behaves towards solutions of alkalies just as the solutions of acid salts do, and on evaporating down, a normal salt is obtained—

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

It has already been stated that chromium may take the place of aluminium in the composition of an alum (p. 133).

CHAPTER XIV

THE KINETIC MOLECULAR THEORY

In the preceding chapters we have learned that each chemical substance is made up of molecules all alike amongst themselves, which in their turn are composed of atoms of elementary bodies combined together in definite numbers; and it has been indicated how we may obtain information concerning the relative masses of these atoms and molecules. We have further seen that all chemical change is merely a rearrangement or redistribution of the atoms of the original molecules taking part in the actions, with consequent formation of new molecules; and what the general conditions are under which such chemical change may take place. But as yet we have formed no conception of the mechanical constitution of substances and of the mechanism of chemical change; in other words we have not yet considered how the molecules go to build up the whole,—whether they are at rest or in motion, whether in the different states of matter there is a difference in the state of the molecules, nor how this state may affect the chemical rearrangement of the atoms.

It is plain that the kind of matter most suitable for study from this point of view is matter in the gaseous state, for, in this form, substances obey laws which in point of simplicity and extensive application are not approached by substances in either of the other states of

aggregation. We have the simple laws of Boyle, Charles, and Avogadro, which connect together in a perfectly definite manner the pressure, temperature, volume, and number of molecules in all gaseous substances, whatever their chemical nature or other physical properties may be. These general laws at once point to great simplicity in the mechanical structure of gases, and to the sameness of this structure in all cases.

Various hypotheses have from time to time been put forward to explain the behaviour of gases, but only one has been found satisfactory and applicable also, to some extent, to the other states of matter. This hypothesis is called the **kinetic theory of gases**, and is, in its present form, chiefly due to the labours of Clerk Maxwell and Clausius. According to this theory the particles of a gas—which are identical with the chemical molecules—are practically independent of each other, and are briskly moving in all directions in straight lines. It frequently happens that the particles encounter each other, and also the walls of the vessel containing them; but as they are supposed to behave like perfectly elastic bodies, there is no loss of their energy of motion in such encounters, merely their directions and relative velocities being changed by the collision.

The pressure exerted by a gas on the vessel containing it, is due to the impacts of the gas molecules on the walls of the vessel. On this hypothesis of the nature of gaseous pressure we can easily account for Boyle's law, which states that, for a given quantity of any gas, the pressure is inversely proportional to the volume, or what is the same thing, directly proportional to the absolute density. If a mass of any gas contained in a given volume exerts a certain pressure at a definite temperature, then, if we double the number of particles of that gas in the given volume without changing the temperature, the number of impacts on the walls will also be doubled. But doubling the number of particles in a

fixed volume is doubling the density (p. 87); and doubling the number of impacts on the walls is, according to the kinetic theory, doubling the pressure; so that here the pressure is proportional to the density. Not only can we deduce Boyle's law directly from the kinetic theory, but we can also see why gases at high pressures no longer obey this law exactly (p. 80). When the pressure is high, the gas particles get packed closely together, which on the one hand occasions a diminution in the strength of the single impacts on account of the attraction exercised by the particles on each other when thus brought into comparative proximity, and on the other hand an increase in the number of impacts on account of the volume of the particles beginning to bear to the whole volume occupied by the gas a proportion which can no longer be neglected.

It is easy too to see what relation subsists between the temperature and the moving particles. The pressure of a given mass of gas contained in a fixed volume is found to increase as the temperature is raised (p. 77). Now if no chemical decomposition takes place when the temperature is raised, the number of particles remains the same, so the increase of pressure can only be caused by the increased speed of the particles, in virtue of which each particle not only hits the walls oftener, but hits them harder. In a gas at a particular temperature it is not to be supposed that all the molecules are moving at the same rate; for even though all started at the same speed they would, owing to their frequent encounters, soon be moving at different rates. There is, however, a certain velocity with which more particles are moving than with any other velocity, and at speeds diverging from this mean on both sides, we find fewer and fewer particles moving the further from the mean we go.

We have just seen that the temperature of a gas depends on the speed of its particles: since, however,

the particles are not all moving at the same rate, the temperature of the gas which we actually observe must be an average or mean temperature. Some of the gaseous molecules—those moving at speeds greater than the mean speed—have a higher temperature than this average; others, moving at speeds less than the mean speed, have a lower temperature. From considerations connected with the energy of motion of the particles of different gases it can be shown from the theory that all gases must expand by the same fraction of their volume when heated through the same range of temperature; and that they must contain the same number of particles (molecules) in equal volumes if the temperature and pressure are the same.

The laws of Boyle, Charles, and Avogadro follow therefore as direct consequences of the kinetic theory of gases; which justifies us in looking on this theory as a serviceable one. It readily explains too the phenomena of gaseous diffusion. If a strongly smelling gas is liberated at one spot in the perfectly still atmosphere of a room, it is not long before the smell is perceived in the most remote corners of the apartment. In general, when two gases are brought into contact at the same pressure, they at once begin to mix with each other, no matter how different their densities may be. This is caused by the particles of both gases moving rapidly about in all directions. Suppose the two gases are hydrogen and bromine vapour, and that they are contained in a tall cylinder, the bromine vapour forming at first a layer on the bottom. Notwithstanding the fact that the bromine particles are eighty times heavier than the hydrogen particles, the coloured vapour will soon be seen to rise in the cylinder against gravity on account of some of the bromine molecules constantly flying upwards, and of some of the hydrogen molecules flying downwards. After the mixture has attained the same composition in every part, there is no further apparent change; but the

motion of the particles, and consequently the mixing process, goes on as before, only now the further mixing does not alter the composition.

The kinetic theory may likewise be applied directly to the study of the processes of vaporisation and condensation. In a liquid the molecules have not the same independence and freedom of motion as gas molecules. A gaseous substance, in virtue of this freedom of its molecules, can expand so as to fill any space presented to it. A liquid does not do so, but retains its own proper volume, although its molecules still possess sufficient independence to slide easily over one another, and thus enable the liquid to accommodate itself to the shape of the vessel containing it. In spite of this clinging together of the liquid molecules, it happens that some of them near the surface have sufficient motion to free themselves from their neighbours, and, leaving the liquid altogether, to become gas molecules. If these gas molecules may move away unhindered, other molecules from the liquid will take their place; and so the liquid will go on giving off gas molecules until all has evaporated. If, however, the liquid is kept in a closed space, the gas molecules which leave its surface will be able to proceed no further than the walls of this space, and must then return in the direction of the liquid. It will consequently happen that some of them will strike the surface of the liquid again and be retained by it. But liquid molecules still continue as before to become gas molecules and leave the surface of the liquid, so that at one and the same time there are molecules entering and molecules leaving this surface. When in a given time as many molecules leave the liquid as are reabsorbed by it, no further apparent change takes place—the quantities of the liquid and of the vapour remain the same. A state of balance or equilibrium has thus been reached and we may look now at what conditions this state. The number of molecules leaving the liquid depends on

the temperature, for it is only those molecules with greatest energy of motion that will succeed in freeing themselves ; and the motion of the molecules of a liquid, like those of a gas, depends directly on the temperature. The number of molecules reabsorbed by the liquid depends on the number of gas molecules striking the surface of the liquid in a given time, that is, on the number of molecules contained in a given space and on their speed. As we have seen, this number and the speed together determine the pressure exerted by a gas, so the number of molecules reabsorbed depends on the pressure. Temperature thus regulates the number of molecules freed, and gaseous pressure the number of molecules bound ; consequently for each state of equilibrium, when these two numbers are equal, a definite temperature will correspond to a definite gaseous pressure of the vapour in contact with the liquid, or vapour pressure of the liquid, as it is shortly termed. Every liquid has, therefore, at each temperature a definite vapour pressure, and this vapour pressure increases as the temperature rises. The temperature at which the vapour pressure is just greater than the pressure of the atmosphere is said to be the boiling-point of the liquid, for then the pressure of the gas molecules given off is sufficient to overcome the pressure of the atmosphere and to move the air bodily from the surface of the liquid, with the result that free vaporisation or boiling goes on.

It should be noted that, as it is the molecules with greatest energy of motion, *i.e.* with highest temperature that leave the liquid, the average temperature of the liquid must sink as evaporation goes on, unless heat is supplied from an external source.

Experiment 33.—Pour a few drops of ether on the back of the hand and on the bulb of a thermometer. Observe that the hand at once experiences a sensation of cold, and that the mercury in the thermometer sinks. This is due to the fact that ether at the ordi-

nary temperature evaporates rapidly, and being cooled in consequence, abstracts heat from the bodies with which it is in contact.

If at a certain temperature the gaseous pressure of a vapour above the corresponding liquid is greater than the vapour pressure of the liquid at that temperature (that is, greater than the gaseous pressure of vapour which would be in equilibrium with the liquid at the temperature considered), then more molecules will strike the surface and be absorbed by the liquid than will be liberated from the surface, and, therefore, on the whole, condensation of the vapour will go on. Should no liquid be present, but the gaseous pressure of the vapour still be greater than the vapour pressure which the liquid would have at the given temperature, it depends on not very clearly defined circumstances whether condensation will occur or not. So long as the liquid is absent, there is no question of equilibrium at all, for the vapour represents only one side of the balance: it is only when a liquid particle is introduced that the vapour is not in equilibrium with the liquid. The formation of liquid particles in such a vapour as we are discussing seems to depend in a great measure on whether there is a nucleus present on which they may be deposited. Fine dust particles serve as such nuclei in the atmosphere. If air perfectly free from dust particles, and contained in a vessel carefully cleaned inside, is supercharged with water vapour (*i.e.* contains more water vapour than corresponds to the vapour pressure of water under the given conditions), no condensation will in general take place; but the introduction of a few dust or water particles immediately causes deposition of liquid water, and this deposition goes on until the gaseous pressure exerted by the water vapour is equal to the vapour pressure of water at the temperature of experiment.

The particles of solids have not even the freedom of

motion possessed by the particles of liquids, and can in general greatly alter their relative positions. There is no sharp line of demarcation, however, between solids and liquids in this respect, the two classes gradually merging into each other through viscous liquids (syrups etc.) on the one hand, and on the other hand solids such as cobbler's wax, which behave towards moderate external pressures just as liquids do, except that the time required to bring about the change of form is very much longer. Some solids give off particles of vapour in precisely the same way as volatile liquids. Camphor and ice are examples of such solids. It may be frequently observed that snow disappears from the ground in hard frosts if there is any wind blowing. This is on account of the snow (ice) having a small vapour pressure of water vapour even at these low temperatures. The wind removes the small quantity of water vapour lying over the surface of the snow, which then gives up a fresh quantity to restore the equilibrium. This is in its turn removed, and so the process goes on until the snow has altogether disappeared without at any time being melted.

CHAPTER XV

MASS ACTION AND DISSOCIATION

THE kinetic molecular theory was applied in the preceding chapter to the study of the physical phenomena of evaporation and condensation. We saw that at a fixed temperature a liquid was in equilibrium with its vapour only when the latter had a certain gaseous pressure; if this pressure was exceeded, the vapour became condensed to liquid; if the gaseous pressure did not reach the requisite value, part of the liquid evaporated, and thus increased the vapour pressure. It should be noted that the state of equilibrium between the liquid and the vapour was not conceived as a state of absolute repose, the liquid molecules remaining liquid, and the gaseous molecules remaining gaseous; but rather as a state of kinetic or mobile equilibrium, as many gaseous molecules becoming liquid in a given time as there were gaseous molecules produced by the liquid in the same time. In other words, we imagined a continual give and take process to be going on between the vapour and the liquid, and this did not cease when the two were in equilibrium, but went on as before; only now the exchanges were equal, and consequently no difference could be noted, for individual exchanges escape our observation. This conception of a kinetic equilibrium is extremely important to the chemist, for it can be applied not only to cases in which two forms

of the same substance change into each other, but also to the case where two different substances, or sets of substances, are transformed one into the other, *i.e.* to chemical reactions. As states of equilibrium or balance form the present subject of our consideration, the chemical reactions we study from this point of view belong to a particular type, and may be called **balanced actions.**

When sugar is heated, as in Experiment 3, p. 7, the products of the decomposition which takes place cannot be brought to recombine in order to form the original sugar. The sugar which has been transformed is changed once and for all—the decomposed molecules remain decomposed. Here there is no question of kinetic equilibrium—the action is not a balanced one. On the other hand, if water vapour is heated to a sufficiently high temperature, it is decomposed into oxygen and hydrogen. But we know that at a temperature below that sufficient to effect the decomposition of water vapour, oxygen and hydrogen combine to form water. At intermediate temperatures we might expect both of these reactions to go on simultaneously, water being decomposed into oxygen and hydrogen on the one hand, and oxygen and hydrogen uniting to form water on the other hand. This is actually what occurs. At a definite (high) temperature and pressure there are quantities of water vapour and of oxygen and hydrogen which are in equilibrium with each other. The name **dissociation** is given to such balanced action as this, where decomposition is effected by heat with formation of gaseous products.

As a simple example of dissociation we may look at what happens as we heat iodine vapour to the temperature at which it is entirely decomposed. Like any other gas, iodine vapour consists of molecules which are in brisk movement in all directions. As we saw in Chapter XIV. these molecules are not all moving at the

same rate, but rather with widely different speeds; and in conformity with this they are at widely different temperatures. Now the molecule of iodine at temperatures not far above that at which iodine is vaporised consists of two atoms, and may thus be represented by the molecular formula I_2. But at a certain much higher temperature, which we may call the temperature of dissociation, the molecule I_2 splits up or dissociates into two new molecules, each of which contains only a single atom of iodine. Suppose then that we begin to heat the iodine vapour. As the average temperature (p. 142) of the whole rises, the temperature of all the molecules rises also, and it will happen as the heating is continued that some of the molecules moving with high speeds will reach the dissociation temperature. The atoms constituting these molecules, besides the motion in a straight line which they possess as parts of the molecules, have also an independent vibratory motion which increases with the former; and when the speed of the molecule as a whole corresponds to the dissociation temperature, the vibrating motion of the component atoms has reached such a pitch that the atoms part company altogether and now behave as molecules on their own account. Let us assume the average temperature to be kept constant for a moment. Some of the I_2 molecules which were under the dissociation temperature will, in virtue of their encounters with the other molecules, acquire a speed corresponding to this temperature, and will therefore dissociate into single atoms. But at the same time, and for the same reason, the speed of some of the iodine atoms will be so far lessened, that when they meet with each other they will combine to form I_2 molecules. Thus at the given temperature there are iodine molecules breaking up into iodine atoms, and iodine molecules being re-formed from iodine atoms. When the number of molecules decomposed in a given time is equal to the number of molecules re-formed in

the same time, there is dissociation equilibrium—the one action, decomposition, then balances the other, recombination.

As the mean temperature of the vapour rises, more and more molecules reach the temperature of dissociation, so that a greater proportion of the vapour is split up into elementary atoms. From what has been previously said, it is easy to see how the rate at which the decomposition proceeds depends upon the temperature. The molecules cluster, as it were, round the mean temperature, a great many molecules having temperatures close to this, but very few having temperatures far removed from it. Thus a change of temperature of 10 degrees, say, when the vapour is far removed from the temperature of dissociation, will only affect a very few molecules; whilst a change of the same amount when the vapour is close to the dissociation point will affect a great many. The rate therefore at which the vapour will dissociate as the temperature rises uniformly, is greatest when its mean temperature, measured by the thermometer, is the real temperature of dissociation.

In order to ascertain the progress of dissociation in such a vapour as that of iodine, it is only necessary to determine the vapour density at the various temperatures. The vapour density should remain constant at all temperatures (p. 83) if the number of molecules in the vapour remains the same. But if some of the molecules decompose into simpler molecules, as actually takes places in the case of iodine vapour, where one molecule having the composition I_2 decomposes into two molecules each consisting of a single atom of iodine, then there will be more molecules present in the same quantity of vapour than if no decomposition had taken place. Therefore by Avogadro's law the volume occupied will be greater and the density less. Suppose the vapour to be heated to so elevated a temperature that all the I_2 molecules are dissociated; then there

will be twice as many molecules present as in the undissociated gas, and the vapour density will therefore only be half as great.

The following table shows the relation between the vapour density and degree of dissociation of iodine vapour at various temperatures. The vapour density corresponding to the molecule I_2 is 254 (density of hydrogen = 2, compare footnote, p. 83).

Temperature.	Vapour Density.	Amount Dissociated.	Increase of Dissociation for 100°.
700°	243	5%	...
800°	237	7	2%
900°	229	11	4
1000°	211	20	9
1100°	194	31	11
1200°	178	43	12
1300°	163	56	13
1400°	152	68	12
1500°	143	77	9

It will be seen that although the dissociation of iodine vapour has already begun at 700°, yet at 1500° it is not complete, only 77% of the vapour being at that temperature decomposed. The last column in the table gives the rate at which the dissociation proceeds as the temperature rises. The rate increases gradually up to 13% for a hundred degrees rise of temperature and then falls off; this indicates that the true temperature of dissociation (p. 150) lies between 1200° and 1300°, where the maximum rate occurs.

Another example of the dissociation of one gaseous molecule into two simpler molecules similar to each other is to be found in the case of nitrogen peroxide, which at ordinary temperatures consists partially of molecules of N_2O_4 and partially of molecules of NO_2. Above 130° only NO_2 molecules exist at the atmospheric pressure.

The kinetic theory throws some light on the influence

of pressure on the dissociation observed in the above cases. It is temperature alone which conditions the dissociation of a molecule of I_2, say, for each molecule can split up independently of its neighbours as soon as it acquires the proper temperature. But if we consider the other side of the balance, that is, the reproduction of I_2 molecules from single atoms of iodine, we see at once that a molecule of I_2 can only be formed when two single atoms encounter each other. Now these atoms will do so the more frequently the more there are of them in a given space. If the temperature is kept constant, and the pressure increased, the number of I_2 molecules decomposed in a given time remains the same as before. On the other hand the I_1 molecules are now packed closer together, and will therefore encounter each other and combine more frequently, that is, the number of I_2 molecules re-formed will be greater than before. On the whole, then, the number of molecules dissociated at any instant under the increased pressure will be smaller than the number dissociated under the original pressure. Thus an increase of pressure here diminishes the degree of dissociation at any temperature. This is illustrated by the following table, which gives the degree of dissociation of nitrogen peroxide at 50°, the pressure being varied.

Pressure in mm. of Mercury.	Degree of Dissociation.
30	92%
100	80
150	72
200	67
300	60
400	54
500	49

What has just been said with regard to the closer packing of the iodine atoms (or of the NO_2 molecules) diminishing the amount of dissociation, is an example of a perfectly general principle regulating chemical actions

in which gases or substances in solution are involved. The closer the reacting molecules are together, the oftener will they meet, and so the opportunity of chemical action between them will be increased. The principle is known as that of **mass action**, and the law may be stated that when any substances in the gaseous or dissolved states enter into a chemical reaction, the amount of the action is proportional to the active mass of each of these substances. By the active mass, or molecular concentration of a substance, we mean the number of molecules of it contained in the unit of space. Of course we do not know, nor do we require to know, the absolute number of molecules in unit space; all we want is the relative number, and this we obtain by dividing the weight of the substance in grams contained in 1 litre by its molecular weight. Thus the active mass is usually expressed as so many gram-molecules per litre, more especially when solutions are dealt with.

The vapour of phosphorus pentachloride PCl_5 was found, above 300°, to have a density only about half that required to correspond with its formula according to Avogadro's law. This fact would indicate that twice as many molecules were present in the vapour as one would have expected (compare p. 150). The explanation of this apparently anomalous vapour density is found in the fact of dissociation taking place under the conditions of investigation. The vapour obtained from the solid pentachloride does not consist of phosphorus pentachloride at all, but of a mixture of an equal number of molecules of phosphorus trichloride and chlorine. Dissociation takes place according to the equation—

$$PCl_5 = PCl_3 + Cl_2,$$

each molecule of the original substance splitting up into two, which, however, in this case are not similar to each other. Just as with iodine, the dissociation diminishes as the pressure is increased. For example, if the pres-

sure is doubled, the active mass of *each* of the two products of dissociation is doubled, so the amount of chemical reaction between them is quadrupled; but the active mass of the decomposing substance, and consequently the amount of decomposition in unit volume, is only doubled. Increase of pressure therefore favours the recombination, and so diminishes the amount dissociated. The dissociation may also be diminished by having one of the products of dissociation present from the beginning. In this way Wurtz volatilised phosphorus pentachloride in an atmosphere of phosphorus trichloride, one of its dissociation products. The active mass of this product was therefore relatively large, and consequently increased the recombination, if we suppose the amount of decomposition in unit volume to remain the same as before; so that the amount dissociated was on the whole diminished. When sufficient trichloride was present, it was found from a consideration of the vapour density of the mixture that the pentachloride was not appreciably dissociated at moderate temperatures.

Another instance of a substance with so-called abnormal vapour density was early observed in ammonium chloride. This salt is easily volatilised, but the molecular weight deduced from its vapour density is only half that which corresponds to the simplest formula which can express its composition, viz. NH_4Cl. The apparent abnormality is due to the fact that the density we observe is not the density of ammonium chloride vapour at all; but of a mixture of ammonia gas and hydrochloric acid gas, the ammonium chloride on vaporisation dissociating according to the equation—

$$NH_4Cl = NH_3 + HCl.$$

Thus for every original molecule we have two molecules in the vapour, which causes the molecular weight to appear only half as great as that of the undecomposed substance. That ammonium chloride dissociates when

vaporised may be easily proved by separating the products of dissociation from each other.

Experiment 34.—A hard glass tube 15 cm. long and 1 cm. in diameter is sealed at one end and held upright in a clamp with the closed end down. The upper portion of the tube is protected from heating by a piece of wire gauze through a hole in the middle of which it is pushed. A small quantity of ammonium chloride (about ·05 g.) is dropped into the tube, the lower end of which is heated with the full flame of a Bunsen burner. A piece of moistened red litmus paper placed at the open end becomes blue after a minute or two. Soon, however, we find on repeating the test that no further alkaline reaction is observed. On now applying a moistened blue litmus paper, it will be turned red.

The alkaline reaction at first observed is due to ammonia gas; the final acid reaction is due to hydrochloric acid gas. The ammonia, being lighter, escapes from the tube more rapidly than the hydrochloric acid; thus in the vapour which first comes off there is excess of ammonia,—in the last portions of vapour there is excess of hydrochloric acid.

Similar methods may be employed for detecting dissociation in other instances. The colour of the gases sometimes affords us the requisite information. The real vapour of phosphorus pentachloride being nearly colourless, its dissociation may be seen from the colour of the chlorine produced. N_2O_4 is much lighter in colour than NO_2, so as we heat the gas we see it become darker owing to the increasing dissociation.

When calcium carbonate is raised to a red heat, it begins to decompose in the sense of the equation—

$$CaCO_3 = CaO + CO_2,$$

forming calcium oxide and carbonic anhydride. As these products of the decomposition recombine when the temperature is lowered, the action is a balanced one,

and we are here dealing with a case of dissociation where one solid, calcium carbonate, gives rise to another solid, calcium oxide, and to a gas, carbonic anhydride. In applying the kinetic molecular theory to the discussion of such actions involving solids, it is assumed that the active mass of each solid is constant throughout the whole reaction, and independent of the quantity of each present.

The rate at which calcium carbonate decomposes depends entirely on the temperature: the rate of the recombination of calcium oxide and carbonic anhydride depends not on the temperature alone but also on the active mass of the gas, which may vary, that of the solid always remaining constant. As we may suppose the dissociation to take place in vacuo, the carbonic anhydride evolved will be pure, and thus its active mass will be proportional to its absolute density (compare p. 81), that is, proportional to its gaseous pressure (p. 87). In order that a state of equilibrium for a given temperature may be reached, it is necessary that the amount of calcium carbonate decomposed in a given time should be equal to the amount re-formed by the combination of calcium oxide and carbonic anhydride in the same time. The first amount is fixed if the temperature is kept constant; the second amount, on the other hand, varies with the pressure of the carbonic anhydride, so that for the re-formation of a certain quantity of calcium carbonate in a given time the pressure of carbonic anhydride must have a certain value. Equilibrium is thus dependent on the pressure of this gas that exists over the solid. At 1040°, the boiling-point of zinc, the pressure of carbonic anhydride necessary for equilibrium is 520 mm. If the pressure is kept less than this by the carbonic anhydride being removed as it is formed, the calcium carbonate will go on decomposing until nothing is left behind but calcium oxide. If, on the contrary, the pressure of carbonic

anhydride is greater than 520 mm., no dissociation will take place, and calcium oxide will continue to absorb carbonic anhydride until all has been converted into calcium carbonate provided the pressure is kept up. It is only when the pressure of carbonic anhydride is 520 mm. that calcium carbonate and calcium oxide, either singly or mixed in any proportions, can exist in equilibrium with this gas at the temperature of 1040°. Should other gases besides carbonic anhydride be present, they have no effect on the dissociation, provided they do not act chemically on the carbonate or its products, and the only alteration which needs to be made in the above statements is the substitution in them of "partial pressure" (p. 161) for "pressure" of carbonic anhydride.

We see here how close an analogy exists between the vaporisation of a liquid or solid, and the dissociation of a solid when one of the products of dissociation is a gas. In both cases the necessary condition for equilibrium is that a certain gaseous pressure of the vapour or gas should be exerted on the vaporising or dissociating substance for every temperature: in the first instance this is the vapour pressure, in the second, the dissociation pressure.

To conclude this chapter we may take an example of mass action experimentally investigated by Deville, in which two different solids and two different gases are involved. Iron, when heated in water vapour, decomposes the water with liberation of hydrogen and formation of an oxide having the formula Fe_4O_5; and if we pass a current of steam over spongy iron which is sufficiently hot, all the iron is converted into oxide, a corresponding quantity of hydrogen being evolved. If, on the other hand, we pass a stream of hydrogen at the same temperature over the oxide thus formed, iron and water vapour are reproduced. The action is therefore a balanced one, and we might expect that for this tempera-

ture there should exist a mixture of hydrogen and water vapour in such proportions that it would neither reduce the oxide nor oxidise the metal. This is borne out by Deville's experiments, for he showed that iron in a confined atmosphere of water vapour was oxidised with evolution of hydrogen, and that this oxidation went on at a particular temperature until the hydrogen had reached a certain pressure relatively to the pressure of the water vapour present, after which no further change took place. The ratio between the final pressures of hydrogen and of water vapour was, at a given temperature, found to be constant, no matter what the original pressure of water vapour might have been. Proceeding in the reverse way, and heating the oxide to the same temperature as before in an atmosphere of hydrogen, Deville found that reduction went on until the pressure of water vapour produced bore the same ratio to the pressure of hydrogen as was observed in the first case. Now the pressures of the gases are proportional to their active masses, so that for a certain ratio of the active masses, or what is the same thing, for a given composition of the gaseous mixture, no change in the solid takes place at a definite temperature,—and this solid may have any composition between the pure metal and the pure oxide without being affected. For different temperatures the composition of the gaseous mixture necessary for equilibrium is different, but to each temperature there corresponds a definite composition.

This example illustrates how a balanced action, which, when all the reacting substances are retained within the system, proceeds only a certain length and then stops,—may by the removal of some of these substances go on to completion in one sense or the other. As we pass a current of steam over the heated iron, the hydrogen evolved is constantly removed, and consequently the pressure of it necessary to establish equilibrium is never reached. The action therefore

proceeds until all the iron is converted into oxide. Conversely, a stream of hydrogen continually passing over the oxide Fe_4O_5 carries along with it the water formed by the reduction, so that there is practically never a pressure of water vapour over the oxide; from which cause the reduction goes on until the oxide is completely reduced. A process, therefore, which might appear at first sight incapable of being reversed, may in reality be a balanced action. If we add sufficient sulphuric acid to a solution of barium chloride, the sulphuric acid liberates the hydrochloric acid completely from the chloride with formation of barium sulphate. In all probability the reaction is a balanced one, only one of the products, barium sulphate, on account of its insolubility, is constantly removed from the sphere of action as it is formed, with the result that the decomposition of the chloride goes on until all has been transformed.

CHAPTER XVI

SOLUTIONS

It has been stated in Chapter III. that one of the essential conditions for the occurrence of a chemical reaction is that the reacting bodies should be in close contact. In the case of solids and liquids it is often difficult to effect a sufficiently intimate mixture. When vigorous chemical action is desired between solids, it is usual to reduce them to as fine a state of division as possible so as to increase the surface of each which will come in contact with the other. An example of this is to be found in gunpowder, the constituents of which —sulphur, charcoal, and nitre—are finely ground previous to being mixed: other examples are the various compositions used in the manufacture of match-tips and of fireworks. Liquids which do not mix, such as oil and water, may have their contact surface increased by brisk agitation; for then one or other breaks up into globules, which present a comparatively large surface in contact with the second liquid.

These methods of mixture, however, are imperfect and of no very wide application; so recourse is usually had to another mode, when substances which are solid under ordinary conditions are required to act chemically on each other. The plan adopted is to dissolve the substances if possible in a common solvent. Then each substance may by stirring be at once uniformly

distributed throughout the whole volume occupied by the liquid. The solution thus obtained is to all mechanical agents perfectly homogeneous, *i.e.* the smallest part we can separate from it by mechanical means has precisely the same composition as the whole. The intermixture of the dissolved substances is therefore very intimate, and so one of the prime conditions for chemical reaction between these bodies is fulfilled.

The process of solution presents, in special instances at least, some analogy to chemical action; but the product—the solution itself—may best be looked upon as a homogeneous mixture, not as a chemical compound. Accordingly, in what follows, we shall treat of solutions entirely from this point of view.

It is always possible to mix any quantity of one gas uniformly with any quantity of another gas. This property of gases is perfectly general, so that we may say, any gas can dissolve any other gas. Of course in the case of gaseous substances (such as hydrogen chloride and ammonia) which react chemically when they come into contact with each other (p. 19), no mixture can, properly speaking, be prepared; for the substances, as soon as they are mixed, cease to exist as such. These are special cases, however; and in general it may be said that there is no indication of chemical action (p. 36) when gases are mixed. Each gas in a mixture retains unchanged all its chemical and physical properties, precisely as if the other gas (or gases) were absent, and it alone occupied the whole volume. In particular, the pressure exerted by each gas in a gaseous mixture is equal to the pressure which that gas would exert under the same conditions did it by itself fill the volume occupied by the whole. This pressure is called the *partial pressure* of the gas; and it at once follows, from the above statement, that the total pressure of the mixture is equal to the sum of the partial pressures of the constituents.

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Gases are very generally soluble in liquids. Mercury is the only instance of a liquid which at the ordinary temperature dissolves no appreciable quantity of any gas. The amount of a gas dissolved by a liquid depends on the nature both of the gas and of the liquid, and varies enormously in different cases. It is usually measured not in parts by weight but in volumes. Thus the "solubility" is expressed by the volume of gas (measured at the temperature and pressure of experiment) which is dissolved by one volume of the liquid. Another expression, introduced by Bunsen, who made the first exact experiments on the solubility of gases, is the "coefficient of absorption," which is simply the above volume of gas reduced to 0° according to Charles's law. A few examples of the solubility of various gases in water are given in the following table.

One volume of water dissolves at 0° and 760 mm. pressure

1050	vols.	Ammonia.
505	,,	Hydrogen chloride.
80	,,	Sulphurous anhydride.
4·4	,,	Hydrogen sulphide.
1·8	,,	Carbonic anhydride.
·04	,,	Oxygen.
·02	,,	Nitrogen.

In the case of the two first gases, a great evolution of heat occurs when they dissolve in water, accompanied by a considerable change of volume. The solution of hydrogen chloride is considerably heavier, and the solution of ammonia considerably lighter than water.

The solubility of a gas in a liquid always diminishes as the temperature is raised, and gases which are only moderately soluble in the liquid may, in general, be expelled completely from solution by prolonged boiling.

Experiment 35.—Heat some tap-water slowly in a test-tube. Long before the water begins to boil, bubbles will be seen forming on the sides of the tube. These

are produced by gases which have been dissolved from the atmosphere at the ordinary temperature, and which separate from solution on account of their diminished solubility at the higher temperature.

1. (The quantity of gas dissolved by a given quantity of a liquid is proportional to the pressure exerted by the gas) (Henry's law); 2 (and in a mixture of gases the amount of each dissolved is proportional to its partial pressure) (Dalton's law). The solubility of a gas in a liquid is thus another example of a property of the gas which is not altered by intermixture with other gases. A second way of stating Henry's law is as follows: 3 (A given quantity of a liquid always dissolves the same volume of a gas independently of the pressure.) For example, if a certain quantity of a liquid dissolves one volume of a gas at a definite pressure; then, according to the first statement of the law, it will dissolve twice the amount if the pressure is doubled, *i.e.* two volumes measured at the original pressure. But doubling the pressure halves the volume of the gas (by Boyle's law), so that the volume of gas measured and dissolved at the increased pressure is $\frac{1}{2} \times 2 = 1$ volume, as before.

These laws are obeyed strictly only at moderate pressures, and by gases which are not extremely soluble. Ammonia, for instance, does not at the ordinary temperature dissolve in water proportionally to its pressure; but at 100°, when it is only sparingly soluble, it obeys Henry's law.

If a gas follows Henry's law, it may be removed from a liquid by placing the solution in a space which is kept exhausted by an air-pump. It is easily seen how this comes about. The pressure over the liquid is nil: so the amount of gas dissolved should also be nil, for this amount is directly proportional to the pressure. Consequently gas escapes from the solution. It is removed, however, by the air-pump without being allowed to exert its pressure on the surface of the liquid. This

occasions a further liberation of gas, which is in its turn removed; and the process goes on until only the pure solvent is left. Precisely the same thing happens if a liquid charged with gas is left freely exposed in an atmosphere of another gas. The pressure of this second gas does not affect the solubility of the first gas at all: it is the pressure of the first gas alone which determines the amount of it dissolved (Henry's law). The only effect of the indifferent gas is to retard the liberation and removal of the dissolved gas; the final result is the same as before, but a longer time is required to bring it about. It is a familiar fact that aerated waters get flat on standing open. This is due to the carbonic acid with which they are charged slowly escaping into the atmosphere, the air being here the indifferent gas. If a current of one gas is passed through the solution of another, then the liberated gas is removed at once from over the surface of the liquid, so that its pressure practically vanishes. This causes the liquid rapidly to lose all its charge of the gas originally dissolved, but at the same time it becomes charged with the second gas, for it is exposed to a continuous pressure of the latter. One gas may thus be made to displace another from solution.

Some liquids mix freely with each other in all proportions, *e.g.* alcohol and water; others do not mix perceptibly, *e.g.* mercury and water; and there is a third class, exemplified by water and ether, which do mix with each other, but only partially. The mutual solubility of most liquids becomes greater as the temperature rises. It is consequently possible that substances which under ordinary conditions only dissolve in each other to a limited extent may at higher temperatures be miscible in all proportions. For example, if we shake up together about equal quantities of water and aniline at the ordinary temperature, the two liquids will form a sort of emulsion, which, however, on standing separates

into two layers, the upper layer being water containing about 1 per cent of aniline, and the lower layer aniline with about 2 per cent of water dissolved in it. If the substances are shaken up at 100°,[1] then it is found that the aqueous solution now contains nearly 4 per cent of aniline, and the aniline solution about 10 per cent of water. At 160° these percentages have increased to 25 and 32 respectively; and at 167° each has attained a value of about 50. The watery solution then contains half its weight of aniline, and the aniline solution half its weight of water; that is, the solutions have the same composition and thus mix freely with each other. We see therefore that aniline and water, which are mutually soluble only to a small extent at the temperature of the air, are miscible in all proportions when the temperature rises above 167°. It is not necessary that the two percentages should both finally attain the same value, as they do in the instance given above. In the case of phenol (carbolic acid) and water, which mix freely above 69°, it is found that at a little below this temperature the phenol is soluble in water to nearly 36 per cent, and the water in phenol to a little less than 64 per cent. All that is required is that the two layers should attain the same composition, which occurs when the sum of the two percentages is 100.

The properties of a mixture of liquids are in general not the sum of the properties of its components, *e.g.* the volume is seldom equal to the combined volumes of the liquids before mixing. In this respect liquids differ from gases, and the mixture presents in some degree an analogy to chemical combination.

Experiment 36.—Take a glass tube about 1 cm. bore and 1 metre long. Close one end and fill the tube half full of alcohol. Then through a narrow tube which reaches to the bottom of the wide one, pour

[1] At temperatures above the boiling-point the liquids must be heated under pressure.

in water cautiously until the alcohol is near the top. Take out the narrow tube and fill up with alcohol. Close the open end now with the thumb, and invert two or three times, so that the liquids may mix. An empty space about 3 cm. long will be found at the top. This is due to the contraction of the liquids on mixing.

Solutions of solids in liquids play the most important part in chemistry, the solvent chiefly employed being water. If a solid is shaken with a liquid for a long time at a definite temperature, a stage is reached after which the liquid will not take up more of the solid substance, however long the two may be left in contact. This corresponds to the case of the partial solution of one liquid in another, *e.g.* aniline in water. While, however, the mutual solubility of nearly all liquids increases with rise of temperature, this is not so with solids,—their solubility may increase or diminish as the temperature rises, or it may remain practically stationary. As a general rule it increases.

A solution which remains unchanged in contact with a solid substance is said to be *saturated with respect to that substance.* This state of saturation holds of course only for a fixed temperature. If the temperature is changed, the substance becomes more soluble, or less soluble, than before. In the first case some of the remaining solid dissolves ; and in the second case some of the solid previously dissolved is deposited. The solution finally becomes saturated at the new temperature. It must be noted that the state of saturation is determined by the presence of undissolved solid in contact with the solution.

The phenomena connected with saturation may best be studied in the special case of solutions of sodium sulphate, which are not only important historically, but are particularly suited for illustration from the number of aspects they present. Sodium sulphate exists as a solid

in three principal forms: first, as the anhydrous salt Na_2SO_4, then as the hydrate, $Na_2SO_4,7H_2O$, and lastly as Glauber's salt, $Na_2SO_4,10H_2O$. The aqueous solutions prepared from these solids are identical if they are of the same strength. If Glauber's salt is dissolved in hot water to form a saturated solution, and if the excess of solid is removed, then the solution thus obtained may be cooled to the ordinary temperature without any change taking place, although the solubility of the salt diminishes on cooling. The solution saturated at a high temperature thus contains when cooled more sodium sulphate than a solution saturated with Glauber's salt directly at the low temperature; it is therefore said to be *supersaturated* with respect to Glauber's salt. As long as there is no solid salt present, it differs in no respect, except strength, from the saturated solution; it is only when a crystal of Glauber's salt is introduced that the difference becomes evident. The crystal, which would have no effect on a saturated solution, immediately causes separation of the solid salt, and this separation continues until the solution becomes saturated. Many supersaturated solutions may be kept for an indefinite period in closed vessels without crystallisation of the dissolved substance taking place. The only certain method of inducing crystallisation is the introduction of a particle of the crystalline substance. Compare with this the behaviour of a liquid in presence of its "supersaturated" vapour (p. 145). All salts are not capable of forming supersaturated solutions: those which contain water of crystallisation (p. 116) do so most readily. Supersaturation, like saturation, must be conceived with reference to a definite solid—a solution in itself can neither be said to be saturated nor supersaturated. It is possible, for example, to prepare a solution of sodium sulphate which, at the ordinary temperature, will crystallise when in contact with Glauber's salt, but which can still dissolve small quantities of the hydrate $Na_2SO_4,7H_2O$.

The solution is therefore at one and the same time supersaturated with reference to Glauber's salt, and unsaturated with reference to the salt $Na_2SO_4,7H_2O$.

Solutions of sodium sulphate present a still further peculiarity. Up to 33° the solubility of the sulphate increases with rising temperature; after passing that point it diminishes. This is best illustrated by the curves given in Fig. 2, in which use has been made of a method of great importance in representing how one magnitude (here the solubility) varies, when another magnitude (here the temperature) assumes different values. Two straight lines are drawn at right angles to each other, and from their point of intersection o we mark off along one of them lengths proportional to one of the magnitudes. Thus in Fig. 2 the horizontal line is divided into equal parts, each representing an interval of 20° of temperature. Then at every temperature (measured along the line) at which a determination of the solubility has been made, we erect a perpendicular of length proportional to the solubility at that point. By joining the tops of these lines—called the ordinates—we obtain a curve which represents approximately the solubility at all temperatures. In the figure the ordinates are not shown, but in their stead we have marked off on the second line equal lengths representing the solubility, *i.e.* the parts by weight of sodium sulphate dissolved by 100 parts of water. From the first portion of the curve we see, for example, that when the abscissa, or length measured along the horizontal axis, is 20, the corresponding ordinate is also 20; that is, at 20° 100 parts of water dissolve 20 parts of sodium sulphate; or the saturated solution of Glauber's salt at 20° consists of 20 parts of sodium sulphate and 100 parts of water. It will be observed that there is a sharp break in the curve at 33°. The reason why this break occurs is that at temperatures above 33° Glauber's salt cannot exist as a solid, but breaks up into anhydrous sodium sulphate and

water. Thus above 33° we can never have a solution of sodium sulphate in contact with a crystal of Glauber's salt, but only with the anhydrous salt. The curve therefore below 33° represents the solubility of Glauber's salt, and above 33° the solubility of the anhydrous sulphate. It consequently consists of two perfectly independent portions

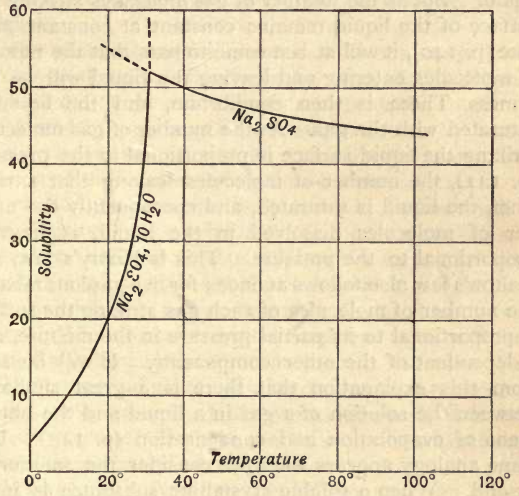

FIG 2

which cut each other at 33°. The solubility of Glauber's salt increases with rise of temperature; that of the salt Na_2SO_4 diminishes. The dotted lines in the diagram represent the true continuations of the two curves, which may be realised under proper conditions of experiment.

The kinetic theory affords a ready explanation of the phenomena of solution. If we take, for example, the case of the solution of a gas in a liquid, we can easily

see that the gas molecules impinging on the surface of the liquid, may be held there by the attraction of the molecules of the solvent. When, however, a number of the gas molecules have accumulated in the liquid, some of them, in virtue of their motion, will fly out from the surface of the solution, and this will happen the more frequently the more molecules there are dissolved in the liquid. But as the number of gas molecules striking the surface of the liquid remains constant at constant pressure (p. 140), it will at last come to pass that the number of molecules entering and leaving the liquid will be the same. There is then equilibrium, and the liquid is saturated with the gas. As the number of gas molecules striking the liquid surface is proportional to the pressure (p. 141), the number of molecules leaving that surface when the liquid is saturated, and consequently the number of molecules dissolved in the liquid, is likewise proportional to the pressure. This is Henry's law, and Dalton's law also follows at once ; for in a gaseous mixture the number of molecules of each gas striking the surface is proportional to its partial pressure in the mixture, and independent of the other components. It will be seen from this explanation that there is a great similarity between the solution of a gas in a liquid and the phenomena of evaporation and condensation (p. 143). The same analogy appears when we consider the solution of a solid. When a soluble crystalline substance is introduced into a solvent, some of its particles become detached and enter the solvent. After a time certain of these detached particles come into contact with the solid again, and are retained by it. This give and take process goes on until the same number of particles leave the solid and return to it in a given time. No further apparent change then takes place, and the solution is saturated. The number of particles which return to the solid evidently depends on the number of them contained in unit volume of the solution, *i.e.* on the strength or

concentration of the solution. If the solid is brought into contact with a stronger solution than the above, more particles will enter the crystal than will leave it, and so the crystal will increase in size. Such a solution is supersaturated with regard to the solid. In a weaker solution fewer molecules will come into contact with the solid and be retained by it than will leave it, *i.e.* the solution is unsaturated and the crystal will dissolve, in part at least.

The phenomena of diffusion in solutions are precisely similar to those we observe in the case of the diffusion of gases (p. 142). If we place a layer of the solution of a coloured salt, such as copper sulphate, on the bottom of a cylinder, and fill this up carefully with water, then in spite of the solution being denser than the pure water, the colour of the copper sulphate will be observed to ascend slowly in the cylinder. This process of diffusion will go on until the copper sulphate is uniformly distributed through the whole bulk of the water. Here, however, the diffusion is incomparably slower than it is in gases. While bromine vapour and hydrogen will have formed a uniform mixture in an hour, it will take years for the copper sulphate solution to become everywhere of the same strength, if the vessel in which it is contained is protected from mechanical disturbance and from sudden change of temperature.

We have already stated that solutions may in general best be considered not as chemical combinations, but as homogeneous mixtures, the different components of which retain many of their properties unchanged. The solvent may for most purposes be supposed not to influence the dissolved substance at all, so that in studying the latter we may neglect the solvent altogether. This may be done especially in the case of weak solutions. If we confine our attention to the dissolved molecules in dilute solutions, and compare their condition as a whole with the different states of aggregation (Chapter I.), we

see that this condition presents a close analogy to the gaseous state. The dissolved molecules are not within the range of each other's attraction, as are the molecules of solids or liquids, but are comparatively widely sundered, and only encounter one another occasionally, just as in the case of gases. Now this similarity of state might lead us to suspect some analogy between the behaviour of dissolved substances in dilute solution, and of substances in the gaseous state. Such an analogy in fact exists, but it was only in 1887 that Van 't Hoff succeeded in showing how close and far reaching the analogy really is. This he did by introducing the conception of **osmotic pressure**, which in solutions corresponds to gaseous pressure in gases and vapours. An idea of the nature of osmotic pressure, and the relation between it and gaseous pressure, may be obtained from a consideration of the following imaginary experiment. We have seen (Chapter IV.) that palladium has the power of absorbing hydrogen at low temperatures: on heating strongly, this hydrogen is again given up. In virtue of this power, palladium heated to a sufficiently high temperature allows hydrogen to pass freely through it, but is quite impervious to any other gas. Now we may suppose a closed vessel to be constructed of palladium, heated to the requisite temperature, and filled to such an extent with nitrogen that a manometer in connection with it registers a pressure of half an atmosphere within the vessel. Let the apparatus be immersed in hydrogen. The palladium walls will allow hydrogen to pass in through them, but will not permit the nitrogen already inside to escape. Hydrogen should enter the vessel until its pressure inside and outside is the same, as we can easily see by making a simple application of the kinetic theory. If the pressure of hydrogen outside is equal to 1 atmosphere, then the pressure inside will be $1\frac{1}{2}$ atmosphere as registered by the manometer, for it is made up of 1 atmosphere of hydrogen and $\frac{1}{2}$

atmosphere of nitrogen. The gaseous mixture inside is a solution of nitrogen in hydrogen, and the osmotic pressure of the dissolved substance is the excess of the internal pressure over the external pressure, *i.e.* $1\frac{1}{2} - 1 = \frac{1}{2}$ atmosphere. But the gaseous pressure of the nitrogen is also $\frac{1}{2}$ atmosphere, so here the osmotic pressure of the dissolved nitrogen is equal to its gaseous pressure. If we begin with different quantities of nitrogen in the same vessel, this does not affect the final result —the osmotic pressure is always equal to the (partial) gaseous pressure of the gas originally present. Now, according to Chapter IX., the gaseous pressure is proportional to the density, which, being the amount of matter contained in unit volume, is equivalent to the concentration as defined on p. 153. Consequently the osmotic pressure of the dissolved nitrogen is proportional to the concentration of the solution.

The behaviour of liquid solutions is quite analogous. Let us take for consideration a solution of sugar in water. It is possible to prepare a membrane which allows water to pass freely through it, but which is quite impervious to sugar. Such a "semi-permeable" membrane may be deposited on a strong porous vessel, which, when filled with sugar solution, closed, and connected with a manometer, corresponds to the palladium vessel in the case previously studied. If this porous cell be now immersed in water, the internal pressure shown by the manometer will increase slowly until it attains a certain value above which it will not rise. The excess of this internal over the external pressure is the osmotic pressure of the solution. As in the case of gases it is found to be proportional to the strength or concentration of the solution; *i.e.* if we double or treble the quantity of sugar in the cell, the osmotic pressure will be doubled or trebled. This may be termed Boyle's law for solutions; for the osmotic pressure being directly proportional to the concentra-

tion (which in solutions corresponds to density in gases), it is inversely proportional to the volume of the solution containing a given quantity of dissolved substance. But the resemblance to gases does not stop here. The osmotic pressure is proportional to the absolute temperature if the volume is kept constant; or, the volume of the solution containing a fixed quantity of dissolved substance is proportional to the absolute temperature if the osmotic pressure is kept constant. This is Charles' law for dilute solutions. Further, the osmotic pressure of any given solution is equal to the gaseous pressure which the dissolved substance would exert were it contained as a gas in the volume occupied by the solution at the temperature of experiment. Sugar cannot actually be obtained as a gas, but by making use of Avogadro's law we may calculate what pressure it would exert under given conditions if it could be gasified. All the above laws apply to solutions of other substances besides sugar, and to other solvents than water. Since, therefore, in particular, the osmotic pressure of the different dissolved substances is equal to their gaseous pressure under the same conditions, and since these gaseous pressures are regulated by Avogadro's law (p. 89), it follows that dissolved substances obey a perfectly analogous law, which may be called Avogadro's law for solutions. These laws are only strictly true for dilute solutions, and consequently for moderate osmotic pressures, in the same way as the laws for gaseous substances are only strictly true for moderate gaseous pressures.

We saw in Chapter X. that by employing Avogadro's law we were in a position to determine the molecular weights of gaseous substances by simultaneous measurements of their absolute density, temperature, and pressure. Similarly we may arrive at the molecular weights of dissolved substances by measuring the concentration, temperature, and osmotic pressure of their solutions.

In practice the osmotic pressure is never determined directly for the purpose of fixing molecular weights, as it is a difficult and inconvenient magnitude to measure. Instead of it we measure quantities that are proportional to it, the chief of these being the depression of the freezing-point and the elevation of the boiling-point of solutions. It is well known that an aqueous solution, such as strong brine, boils at a higher temperature, and freezes at a lower temperature than pure water. Now this rise of the boiling-point and sinking of the freezing-point are subject to perfectly determinate laws, both of them being proportional to the osmotic pressure of the solution. As they are easy to determine, especially the latter, molecular weights are now very generally ascertained by observations of the freezing-point of solutions containing a known quantity of the substance under investigation. The molecular weights thus found are in general identical with those obtained from vapour density measurements; that is, the weight of the molecule of a substance as a gas is the same as the weight of its molecule in dilute solution. There is one very important class of exceptions to this rule however: the molecular weights of salts, strong acids, and strong bases in aqueous solution being all smaller than vapour density determinations and general chemical analogies would lead us to expect. An explanation of how these substances come to be exceptional will be given in the next chapter.

CHAPTER XVII

ELECTROLYSIS

WHEN a stick of zinc is dipped into dilute sulphuric acid, zinc sulphate is formed and hydrogen gas is given off from the surface of the zinc (p. 29). This only happens when the zinc is not pure; the freer the zinc is from admixture with other metals the more slowly is it attacked by the acid, and we have reason to believe that perfectly pure zinc would not be attacked at all, however long the two substances might remain in contact. Platinum is not attacked by dilute sulphuric acid under any circumstances. Yet if we put a rod of the purest zinc we can obtain and also a rod of platinum into dilute sulphuric acid, and join those ends of the rods which are not immersed in the acid by means of a metallic wire, we find that chemical action at once takes place, hydrogen being rapidly evolved from the surface of the platinum, not as before from the surface of the zinc. When we investigate what further chemical change has taken place, we find that the platinum has not been attacked in any way, but that part of the zinc has been dissolved by the acid with formation of zinc sulphate. Thus the chemical action is the same as that occurring when (impure) zinc alone is dissolved in dilute sulphuric acid; only the hydrogen is now given off at the surface of the platinum, and not at the surface of the zinc. There are other differences, however, besides this. The

wire connecting the two metals becomes warm, and we can discover by suitable means that an electric current is passing through it. If the wire is cut, the evolution of hydrogen ceases; and if the chemical action is in any way stopped, the current ceases to flow. There is thus an intimate connection between the electrical current and the chemical action. Part of the energy obtainable when zinc is dissolved in dilute sulphuric acid, and which under ordinary circumstances is given out as heat, is under the above conditions converted into electrical energy, and the current so obtained may be made use of in various ways (compare Chapter IV.). The arrangement here described is a simple example of a galvanic cell, by means of which a current of electricity may be produced; it is not a practical form as it stands, but by slight modifications it may be made into an efficient cell.

When a current obtained from a battery of such cells, or in any other way, is passed through a stout platinum wire, and if the wire be cut and its ends immersed in a vessel containing dilute sulphuric acid, oxygen will be given off at one of the ends and hydrogen at the other. That end of the wire connected with the platinum rod of the cell (or the corresponding part of another galvanic element) is called the positive pole, and at it the oxygen is given off: the other end, connected with the zinc, is termed the negative pole—at it the hydrogen is evolved. Such a process of chemical decomposition by means of an electric current is called **electrolysis**. The poles are called the electrodes, the positive electrode being also termed the anode, and the negative electrode the cathode.

On comparing the quantities of gas evolved at the different electrodes, we find that the volumes are such as would be produced by the decomposition of water, *i.e.* for every volume of oxygen given off at the anode there are two volumes of hydrogen produced at the cathode. It would thus appear as if the electric current directly

decomposed water into oxygen and hydrogen. Water alone, however, is not affected by an electric current, for it acts practically as a non-conductor, allowing no electricity to pass through it at all. The addition of sulphuric acid or of some other similar substance is necessary for the current to flow and the decomposition to take place. It was formerly thought that the acid merely "made the water conduct," and was not itself directly affected, but recent investigation has made it extremely probable that while the acid really conducts the electricity, the water is not decomposed directly but in virtue of secondary reactions. When we take moderately strong hydrochloric acid solution instead of dilute sulphuric acid, we no longer get oxygen at the anode, but chlorine; and if nitric acid is taken, nitrous fumes (oxides of nitrogen) are evolved. With a solution of potassium sulphate, oxygen is given off as before at one pole and hydrogen at the other, but round the anode the solution, which was at first neutral, has become acid, and round the cathode it has become alkaline. If a solution of cupric sulphate is taken, copper is deposited on the cathode, and oxygen is evolved at the anode, the solution in the neighbourhood of this electrode becoming strongly acid. From these examples we see that the products of the electrolysis vary according to the nature of the substance dissolved in the water.

The quantity of a compound decomposed is proportional to the quantity of electricity passed through the electrolytic liquid. Thus if we pass a constant current through dilute sulphuric acid, the quantity of gas given off will be proportional to the time the current flows. We have evidently here a means of measuring quantities of electricity and strength of current, for we have only to measure the amount of gas given off in order to obtain the quantity of electricity which has passed through the liquid, and by noting in addition the time the current has flowed, we can calculate the average current strength.

The gas voltameter is an instrument constructed for the purpose of measuring currents in this way.

When the same quantity of electricity is passed through different electrolytic solutions, the quantities of the compounds decomposed, and of the products of decomposition, are in definite proportions by weight; and if the products are gases, these are evolved in simple proportions by volume. For instance, if the same current be passed simultaneously through dilute sulphuric acid and strong hydrochloric acid solutions, oxygen and hydrogen will be given off in the first electrolytic vessel, and chlorine and hydrogen in the second. The gases may be all collected separately, and measured, due allowance being made for the quantities of them dissolved in the liquids. It will be found that the volume of hydrogen given off in the two vessels is the same, and that this volume is equal to the volume of the chlorine and double the volume of the oxygen. From this it follows that the weights of the gases are in the following proportions (Chapter X.)—

Oxygen.		Hydrogen.		Chlorine.
8	:	1	:	35·5

Now these are the proportions by weight and by volume in which hydrogen combines with oxygen to form water and with chlorine to form hydrochloric acid. We find similar relations to exist with other substances. A current which liberates 1 gram of hydrogen from a solution of sulphuric acid will deposit 108 grams of silver from the solution of any silver salt. Here the ratio between the amounts liberated by the same quantity of electricity is the ratio of the atomic weights. The quantities of the products of electrolysis liberated from different electrolytic liquids by the same current are called the *electrochemical equivalents* of these products. These electrochemical equivalents are referred to that of hydrogen as unity. The numbers expressing them in terms

of this unit stand in intimate and simple relations to the atomic or formula weights of the products. The statements of this paragraph are embodied in Faraday's law of electrolysis (p. 194).

One element may have more than one electrochemical equivalent. For every gram of hydrogen produced in a voltameter, 31·5 grams of copper are deposited from the solution of a cupric salt in the same circuit, but twice as much, or 63 grams, from the solution of a cuprous salt. The electrochemical equivalent of copper in cuprous salts is thus twice as great as that of copper in cupric salts.

We may now look for a moment at the modes in which electricity may be transported from one place to another, and endeavour to find a reason for the close relation between the quantity of electricity passing through an electrolytic solution and the amount of chemical action taking place, *i.e.* the amount of substances transformed. Electricity may be made to move from one place to another in two different ways: it may either flow, like water through a pipe, or it may be carried, like water in jugs. In other words it may travel *through* matter, or it may travel *with* matter.[1]

The first case is illustrated by the flow of a current of electricity through a metallic conductor—the electricity moves but the conductor does not, just as water moves but the pipe conducting it remains stationary.

The current in an electrolyte corresponds to the second case: here the electricity is associated with and carried by definite quantities of matter. The carriers of electricity are called *ions*, two sorts of them being always present in an electrolytic liquid. One set of them, the negative ions or anions, move towards the anode; the other set, the positive ions or cations, move towards the cathode. The negative ions carry negative, and the positive ions positive, electricity. Hydrogen, the metals, and metallic radicals, such as ammonium,

[1] Lodge, *Modern Views of Electricity*, p. 66.

form positive ions; salt radicals and the group OH, hydroxyl, form negative ions. We thus see what sort of substances when dissolved in water confer on it the property of conducting electricity: they are substances composed of the ions just mentioned, *i.e.* salts, acids, and bases. Hittorf summed this up in the following statement, "Electrolytes are salts," the term salt here including acids (hydrogen salts) and bases (salts in which hydroxyl is the salt radical). Some substances make the water conduct much better than others. These are called good electrolytes and consist of the strong acids, strong bases, and nearly all metallic salts. Weak acids and weak bases are poor electrolytes. The greater or less power of an electrolytic solution to conduct electricity has no effect whatever on the amount of the dissolved electrolyte decomposed by a given quantity of electricity. Faraday's law is true for the worst electrolytic conductors as well as for the best.

Although aqueous solutions form by far the largest class of substances capable of electrolysis, solutions of salts, acids, and bases in other solvents may also conduct electrolytically, for instance, the solution of hydrochloric acid in alcohol. Salts fused by heat are sometimes good conductors, *e.g.* the chlorides of silver and of lead. Electrolytic conduction is not exclusively confined to liquids, as the above examples might seem to indicate, but has also been observed in solids and in substances in the gaseous state.

Ions of the same kind carry equal quantities of electricity. A certain definite amount of electricity is, for example, associated with each hydrogen atom that acts as an ion, and this quantity may be taken as the electrochemical unit of electricity. The quantities carried by other ions are either equal to this unit, or are simple multiples of it. This notion of ions charged with definite quantities of electricity enables us to see why there is so close a connection between the amount

of electricity passed through a solution and the quantity of the decomposition products formed. As has been already stated, the ions are either atoms or groups of atoms. For instance in a solution of hydrochloric acid they are H and Cl, each charged with an electrochemical unit of electricity, positive in the case of hydrogen and negative in the case of chlorine; in potassium sulphate solution they are K and SO_4, each potassium atom being charged with one unit of positive and each SO_4 group with two units of negative electricity; in a solution of cupric sulphate we have Cu ions and SO_4 ions, charged with two units of electricity each, positive on the copper and negative on the SO_4 ions. Now these ions move towards the opposite electrodes, the positive ions travelling to the negative electrode, and the negative ions to the positive electrode. When they reach the electrodes they lose their charges of electricity, and the discharged atoms or radicals are then in a position to enter into chemical action or to appear in the free state. In the case of aqueous hydrochloric acid, for example, the hydrogen ions when they give up their charge combine with one another in pairs, and come off as hydrogen gas, H_2; at the other electrode, the discharged atoms of chlorine may similarly combine, with formation of chlorine gas Cl_2, or if the solution is weak they may enter into chemical reaction with the water, thus

$$4Cl + 2H_2O = 4HCl + O_2,$$

hydrochloric acid being reproduced and oxygen evolved. In cupric sulphate solution, the copper on losing its charge is simply deposited as metallic copper on the electrode, while SO_4 interacts with the water as follows—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

Sulphuric acid is thus formed at the anode with simultaneous liberation of oxygen. Precisely the same re-

action goes on at the anode in a potassium sulphate solution; at the cathode the discharged potassium atoms decompose water with evolution of hydrogen and formation of potassium hydroxide, thus

$$2K + 2H_2O = 2KOH + H_2.$$

The solution at the cathode therefore becomes alkaline, and the solution at the anode, acid. As the quantity of hydrogen formed is just sufficient to combine with the liberated oxygen to form water (p. 179), it follows that the amount of potassium hydroxide produced at the cathode will be exactly the quantity necessary to neutralise the sulphuric acid at the anode, as a consideration of the above equations will show. These examples suffice to show how the quantities of the decomposition products formed at the electrodes are connected with the quantities of the ions discharged, and consequently with the quantity of electricity passing through the electrolytic solutions.

It still remains to be seen how the ions are produced. At first it was thought that the ions only came into existence when the current passed through the solution, *i.e.* that the current itself split up the salt, potassium chloride, say, into potassium ions and chlorine ions, which were then available for the transport of electricity. Now, this splitting up of a chemical compound would involve some transformation of energy (Chapter IV.); but it has been shown from very exact experiment that no work is done by the current in splitting up a compound in the solution, and consequently it was assumed, by Clausius (1857), that there must always be some free ions in the solution at any given time. In our example there must always be ready to hand in the solution some potassium atoms and some chlorine atoms, which are charged with electricity, and, when the current passes, move towards the opposite electrodes. The presence of only an extremely small quantity of

such free atoms in the solution at any one time is sufficient to account for the fact of the passage of electricity taking place without work being done in splitting up the compound molecule; for as soon as the first free atoms are removed others will be formed (compare Chapter XV. p. 156). The mode in which this was supposed to come about is as follows. The potassium atoms and the chlorine atoms constituting the potassium chloride in the aqueous solution were not considered by Clausius to be paired off with each other permanently; but some of them were regarded as changing partners in consequence of molecular encounters; there was supposed to be, in fact, to a limited extent a mobile equilibrium such as we discussed in the chapter on Mass Action and Dissociation. A few potassium atoms were at any one time without partners, being in the act of changing from one chlorine atom to another; similarly with the chlorine atoms. The electricity seized on these momentarily free atoms, and thus obtained vehicles for its transport. This hypothesis was satisfactory so far as the mere explanation of the conductivity went; but many other phenomena of electrolytic conduction became known, of which the theory in its original form took no account. It was only in 1887 that Clausius's idea was developed and brought into a quantitative form by Arrhenius, who advanced what is now called the theory of **electrolytic dissociation.**

On this theory not a small proportion of the potassium chloride in solution is split up into potassium and chlorine ions—but almost all the salt, and in very dilute solutions, all. Other salts are similarly split up into the metal and the salt radical; acids into hydrogen and the salt radical; bases into the metal, or metallic radical, and hydroxyl. The hydrogen and metals are charged with positive electricity, the salt radicals and hydroxyl with negative electricity, the two

kinds of electricity being just sufficient to balance each other, so that the solution as a whole exhibits no charge. It must be borne in mind that the charged potassium ions existing in the solution are not at all similar to the free element potassium, whose molecules are not electrically charged and may consist each of several atoms. Free uncharged potassium at once decomposes water, charged potassium ions do not. Similarly a chlorine atom charged with one unit of negative electricity is something very different from ordinary chlorine gas Cl_2, which is not charged. This state of electrolytic dissociation exists in the potassium chloride solution whether it is undergoing electrolysis or not; it is the normal state of the solution. If we dip into it a pair of electrodes, then the potassium ions with their positive charges move towards the negative electrode, while the chlorine ions travel in the opposite direction. At the electrodes the ions lose their charges, and exhibit the properties of ordinary uncharged atoms (pp. 182 and 183).

All salts, acids, and bases in aqueous solution undergo electrolytic dissociation to a greater or less extent, and the laws regulating this dissociation are the same as the laws of gaseous dissociation. As the solution becomes more dilute the dissociation proceeds further. This is in analogy with the dissociation of gases, where decrease of pressure increases the amount of dissociation (p. 152). In solutions we have to deal with osmotic pressure which is proportional to the strength or concentration of the solution. If then we dilute the solution, *i.e.* diminish its concentration and consequently the osmotic pressure of the dissolved substances, we increase the dissociation.

In the case of gases the amount of dissociation was measured by ascertaining the vapour density, from which we could calculate, relatively, the number of molecules in a given quantity of gas. In the case of solutions we can obtain the number of dissolved molecules in a given

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quantity from observations of the freezing-point, etc. (p. 175) of the solutions. We find that in salt solutions there are more molecules dissolved than we should calculate from the quantity of salt contained in them and the formula weight of the salt. The salt must therefore have split up partly at least into simpler molecules. These simpler molecules are the ions, each of which acts with respect to the freezing-point of the solution in which they are contained, just as any other molecule does.

Many other facts are in harmony with the hypothesis of electrolytic dissociation, which, it should be remembered, was advanced to explain the *electrical* behaviour of electrolytic solutions. For instance, it is found that the properties of dilute salt solutions depending on the dissolved substance seem to be made up as the sum of two components, one due to the metal, and the other to the salt radical. This, of course, at once finds its explanation in the dissociation theory, according to which the metal and the salt radical lead an independent existence in the solutions.

Examples of how the theory influences our views of chemical change in dilute salt solutions will be found in the chapter on Double Decomposition (Chapter XIX.).

CHAPTER XVIII

EQUIVALENCE

IN the preceding chapter the electrochemical equivalence of elements and salt radicals was defined. The weights of the various elements and radicals which are equivalent from the point of view of electrolysis are those which move along with and are discharged by the same current, and these weights when referred to the equivalent weight of hydrogen as unity stand in simple relations to the atomic and formula weights. This mode of defining electrochemical equivalence only takes account of the phenomena which occur at the electrodes; we might, with greater generality, define those quantities of various elements and radicals to be equivalent which are charged with the same amount of electricity in solution. A few examples of the relations between the atomic weights and electrochemical equivalents of elements are exhibited in the following table.

TABLE I.

	Electrochemical Equivalent.	Atomic Weight.	Ratio.
Hydrogen	1	1	1 : 1
Chlorine	$35\frac{1}{2}$	$35\frac{1}{2}$	1 : 1
Oxygen.	8	16	1 : 2
Copper (in cuprous salts) . .	63	63	1 : 1
,, (in cupric salts) . .	$31\frac{1}{2}$	63	1 : 2
Silver	108	108	1 : 1
Mercury (in mercurous salts) .	200	200	1 : 1
,, (in mercuric salts) .	100	200	1 : 2
Antimony	40	120	1 : 3
Tellurium (in alkaline solution)	$31\frac{1}{4}$	125	1 : 4

Equivalent weights may be estimated with reference to any property or function, and may be different for one and the same substance in the case of different properties; or even, as we may see from the preceding table, in the case of the same property under different conditions. For example, quantities of various gases and vapours that fill a given space under given conditions of pressure and temperature are equivalent to each other in this particular respect. The equivalent weights thus estimated are identical with the molecular weights of the gases if the same unit is chosen in both cases (Avogadro's law, Chapter X.). The quantities of different acids required to neutralise the same quantity of a base are equivalent in acidimetry, and here again there is a simple atomic relation between the acidimetric equivalents of the various acids (p. 124).

The sense, however, in which one substance is said to be equivalent *chemically* to another is different from all these. Quantities of two substances are chemically equivalent when they can combine with the same quantity of a third substance.

The following tables show the quantities of various elements which combine with a given quantity of another element, and which are therefore chemically equivalent.

TABLE II.

Quantities of elements which combine with 1 part by weight of **hydrogen** to form the compounds named in the first column—

Compounds.	Elements.	Equivalents.
Hydrogen chloride	Chlorine	$35\frac{1}{2}$
Hydrogen bromide	Bromine	80
Water	Oxygen	8
Hydrogen sulphide	Sulphur	16
Hydrogen phosphide	Phosphorus	$10\frac{1}{3}$
Methane	Carbon	3
Hydrogen silicide	Silicon	7

TABLE III.

Quantities which combine with $35\frac{1}{2}$ parts of **chlorine.**

Compounds.	Elements.	Equivalents.
Hydrogen chloride	Hydrogen	1
Chlorine monoxide	Oxygen	8
Sulphur dichloride	Sulphur	16
Phosphorus trichloride	Phosphorus	$10\frac{1}{3}$
Phosphorus pentachloride	Phosphorus	$6\frac{1}{5}$
Carbon tetrachloride	Carbon	3
Silicon tetrachloride	Silicon	7
Cuprous chloride	Copper	63
Cupric chloride	Copper	$31\frac{1}{2}$
Antimony trichloride	Antimony	40
Ferrous chloride	Iron	28
Ferric chloride	Iron	$18\frac{2}{3}$

TABLE IV.

Quantities which combine with 8 parts of **oxygen.**

Water	Hydrogen	1
Chlorine monoxide	Chlorine	$35\frac{1}{2}$
Phosphorus trioxide	Phosphorus	$10\frac{1}{3}$
Phosphorus pentoxide	Phosphorus	$6\frac{1}{5}$
Carbonic oxide	Carbon	6
Carbonic anhydride	Carbon	3
Silica	Silicon	7
Cuprous oxide	Copper	63
Cupric oxide	Copper	$31\frac{1}{2}$
Antimony trioxide	Antimony	40
Ferrous oxide	Iron	28
Ferric oxide	Iron	$18\frac{2}{3}$

In estimating the equivalent weights of the elements with respect to hydrogen, we have taken one part by weight of this element as standard; and when with respect to chlorine and oxygen we have taken the equivalent weights of these elements as given in Table II. as standards. The equivalent weight for any element

determined in this way will be found to be in general the same in Tables II., III., and IV., and also the same as the electrochemical equivalent in Table I. Thus the quantity of an element which combines with an equivalent of hydrogen is in general the same as the quantity which combines with one equivalent of oxygen or of chlorine. It often happens that one element combines with another element in more than one proportion; then it has more than one equivalent weight with respect to that element. A comparison of the equivalents of phosphorus, copper, and iron with respect to oxygen and to chlorine shows that though each element has two equivalents in Tables III. and IV., these equivalents are the same in the two tables. The ratios, too, between the different equivalents of the same element are simple ratios; thus between the two equivalents of copper the ratio is 1 : 2, in the case of iron it is 2 : 3, and for phosphorus it is 3 : 5.

These and similar equivalents are the results of quantitative analysis alone, and are independent of any theory of the structure of chemical compounds. They constitute in fact the experimental basis of the laws of fixed and of multiple proportions, and it was from recognising them that Dalton was led to advance his atomic theory. At first no clear line of distinction was drawn between equivalent weights and atomic weights, both terms being used as practically synonymous. The difference between atomic and equivalent weights, however, made itself felt in the cases where one element had more than one equivalent weight. From the conception of an atom it was clear that an element could only have one atomic weight, so that it became a question in such cases to determine which of the equivalents was the real atomic weight, if indeed any of them were so. The question thus raised was long in receiving a satisfactory solution, but by the means we have indicated in Chapter XI. a consistent system of atomic weights has been arrived at, and we

may now look for a little at the relations which subsist between these atomic weights and the old equivalents.

Take the case of water, for instance. Oxygen combines with hydrogen in the proportion of 8 to 1; its equivalent with respect to that of hydrogen as unity is therefore 8. But the atomic weight of oxygen with reference to hydrogen is 16, and thus equal to twice the equivalent weight. A consideration of the formula of water H_2O shows the same thing. This formula represents 18 grams of water, made up of 16 grams of oxygen and 2 grams of hydrogen. But 16 grams is *two* gram-equivalents of oxygen, which are combined with *two gram-equivalents* of hydrogen; on the other hand, combined with *two gram-atoms* of hydrogen there is only *one* gram-atom (= 16 grams) of oxygen. Consequently, if hydrogen is adopted as the unit in both cases, the atomic weight of oxygen must be twice its equivalent weight. The gram-equivalent of phosphorus in hydrogen phosphide is $10\frac{1}{3}$ (Table II.), but in the gram-molecule PH_3 there are 31 grams of phosphorus, so the atomic weight of phosphorus is thrice its equivalent weight in this compound. In hydrogen chloride HCl the equivalent weight of chlorine is $35\frac{1}{2}$, equal to the atomic weight.

From these examples we may see that there is a connection between the ratio of the atomic to the equivalent weight of an element in its hydrogen compounds, and the number of atoms of hydrogen with which the element in question is combined. The quotient *atomic weight ÷ equivalent weight* for chlorine is 1, and one atom of chlorine combines with one atom of hydrogen. The same quotient for oxygen is 2, and one atom of oxygen unites with two atoms of hydrogen. The quotient for phosphorus is 3, and in hydrogen phosphide we have one atom of phosphorus united to three atoms of hydrogen Thus the ratio of the atomic weight to the equivalent weight gives the number of atoms of hydrogen with which one atom of the element will combine. The same

relation is observed in the compounds of the elements with chlorine and other elements whose equivalent weights are equal to their atomic weights, *i.e.* elements which combine atom for atom with hydrogen. The ratio obtained in this way is called the **valency, atomicity,** or **combining capacity** of the elements. The valency of an element also represents the number of hydrogen atoms with which one atom of it can combine. Elements one atom of which unites with one, two, three, or four atoms of hydrogen, are called univalent, bivalent, trivalent, and quadrivalent respectively; or, on another system of nomenclature, monad, dyad, triad, and tetrad.

From the compounds with hydrogen alone it is impossible to ascertain the valency of all the elements, for many of them do not form hydrogen compounds. In such cases the valency is estimated if possible with respect to some other *univalent* element, for example chlorine. Calcium does not combine with hydrogen, but in calcium chloride it combines with chlorine in the proportion of 1 atom to 2; it is therefore bivalent. Again, titanium does not combine with hydrogen, but its chloride, $TiCl_4$, shows it to be quadrivalent. It does not follow that the valency of an element with respect to hydrogen and to chlorine is always the same (see Chapter XXI.). No atom of any element combines with more than four atoms of hydrogen, but chlorides are known with 5 and 6 atoms of chlorine to 1 atom of the other element, which is then termed pentad or hexad as the case may be.

The valency of an element may, then, be regarded in two different aspects: (1) either as a ratio between the atomic and equivalent weights, or (2) it may be referred directly to the atom and appear as a property of this atom. Taking the last view the valency is the number of univalent atoms with which one atom of the element can unite. It has already appeared from the preceding tables that one element may have more than one equi-

valent, depending on the compound in which it is present; corresponding to this fact an element may have more than one valency. When the valency of an element is spoken of without reference to any particular compound, the maximum valency of that element is usually meant. Thus we say that the metal tungsten is hexad, meaning that it forms compounds of the type WR_6, when R stands for a univalent element. We know, for example, the compound WCl_6, but besides this chloride there are others of the formulæ WCl_5, WCl_4, and WCl_2, in which tungsten is pentad, tetrad, and dyad respectively.

Molybdenum is also said to be hexad, although one atom of it forms no compound with six atoms of any univalent element: $MoCl_5$ is the chloride containing the greatest number of chlorine atoms. However, it forms an oxide MoO_3, and from this oxide its maximum valency is estimated. Oxygen is a dyad element, and one atom of it is consequently equivalent to two atoms of the monad elements, hydrogen or chlorine. Three atoms of oxygen are therefore equivalent to six atoms of chlorine, and so we arrive at the conclusion that molybdenum is hexad in the compound MoO_3. It must here be remarked that this method of estimating the valency of an element from its compounds with other elements which are not themselves univalent, is, unless we possess further information about these compounds, unsatisfactory. The valency of an element with respect to a univalent element or elements is a perfectly definite conception; it is the number of the univalent atoms with which one atom of the element combines. Now, as a univalent atom can only combine with *one* other atom, all the univalent atoms in the molecule must be combined with the atom whose valency is in question. But in compounds of the element with bivalent elements this does not follow; it may be otherwise, unless we are in possession of information to the contrary. Thus in the compound MoO_3 it does not follow of necessity from our conception of valency

that all the oxygen atoms are directly united to the molybdenum atom; one oxygen atom might be united directly only to the two other oxygen atoms, and these then to the molybdenum atom. Unless we possess information as to the way in which the atoms are united to each other, we cannot draw any conclusion as to the valency in the second sense in which the term is used (p. 192). For example, in the compound zinc methyl, ZnC_2H_6, it depends entirely on how we imagine the atoms to be combined, what conclusion we should draw as to the valency of zinc in this compound, on the supposition that carbon is tetrad and hydrogen monad. If all the carbon and hydrogen atoms in the molecule were directly united to the zinc atom, the valency would be $(2 \times 4) + 6 = 14$. This result is highly improbable, for we know of no element with a directly determined valency greater than six. As a matter of fact, we are aware that the hydrogen atoms in zinc methyl are not combined directly with the zinc at all, but only with the carbon atoms, and that these are in direct union with the zinc atom. By means which will be more fully discussed in Chapter XX. we know that two groups CH_3 exist in the zinc methyl molecule, and that each of these groups is univalent, and must therefore be directly combined with the zinc, which is consequently in this compound bivalent.

It has already been pointed out that the electrochemical equivalents of the elements are equal to the chemical equivalents (p. 190). This may be looked upon as the general statement of Faraday's law of electrolysis (p. 180). There exists, too, a species of electrochemical valency which may be defined in two ways precisely analogous to those adopted in defining ordinary valency. The electrochemical valency of an element is (1) the ratio of the atomic weight to the electrochemical equivalent, or (2) the number of electrochemical units of electricity with which it can combine,

i.e. with which it is charged. The chemical and electrochemical valencies are, by Faraday's law, as above stated, numerically equal. Hydrogen and other monad atoms are charged with one unit, dyad atoms with two units, triad atoms with three, and so on.

All that has been said with regard to equivalence and valency of elements and atoms applies equally well to radicals and atomic groups. In the nitrates the salt radical NO_3 is combined with one atom of hydrogen or of a univalent metal: it is therefore a univalent radical. So is NH_4, the metallic radical of the ammonium salts, for it unites with one atom of univalent chlorine and corresponding quantities of other elements or radicals. The radical MnO_4 in the manganates is a bivalent radical; but in the permanganates, *e.g.* $KMnO_4$, where it only combines with one monad atom, it is univalent. The radical PO_4 of the orthophosphates is trivalent, the salts having the general formula R_3PO_4 (compare p. 136).

The definition of valency as the number of univalent atoms (or univalent radicals) with which one atom can combine is evidently only strictly applicable when we know the *molecular weight* of the compound considered in fixing the valency. Aluminium in the chloride $AlCl_3$ is trivalent if the formula $AlCl_3$ represents a molecule of the compound, and is not a mere empirical formula (p. 112). At high temperatures the vapour density corresponds to the molecular formula $AlCl_3$, therefore aluminium is trivalent. But at lower temperatures the vapour density leads to the formula Al_2Cl_6, so that here the aluminium atoms are probably quadrivalent at least, one atom being not only united to three chlorine atoms, but also to the other aluminium atom.

The word "valency" is not only used in the senses in which we have hitherto employed it, but is also made to stand for "unit of valency." For instance, carbon, being quadrivalent, is said to possess four "units of valency," or simply four "valencies." These valencies

are frequently denoted in formulæ by placing dots or short lines in conjunction with the symbol representing the atom. Thus the carbon atom is written $:\dot{C}:$ or $-\overset{|}{\underset{|}{C}}-$ to show that it is quadrivalent or can combine with four univalent atoms. Methane, CH_4, may, then, be written $\begin{matrix} H \\ H \end{matrix} : C : \begin{matrix} H \\ H \end{matrix}$ or $H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$ in this way, and carbonic anhydride $O : C : O$. The short lines joining the symbols of two atoms belong, as it were, to both, and are often spoken of as bonds or links. **Graphic formulæ** such as the above show not only the composition of a molecule but also the manner in which the atoms within it are united to each other. The group CH_3, methyl, is represented thus, $-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$, from which we see that it is a univalent group, having one "valency," which is not "satisfied" by being combined with a monad atom or radical. The molecule of zinc methyl is written graphically as follows to represent that the zinc is combined with carbon directly and not with hydrogen, $H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-Zn-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$. A more concise **constitutional** formula, which expresses the same thing, is $Zn(CH_3)_2$. This shows that there are two methyl groups in the molecule each united to zinc. The question of the arrangement of the atoms in molecules will be treated of in Chapter XX.

It has been a much debated question whether the valency of an element is constant or variable. If we look upon the valency as the number of univalent atoms

with which an atom of the element *can* combine, then we may, if we please, say that it is always constant; but if we consider it as the number of such atoms with which an atom of the element *does* combine, then the valency is undoubtedly in many cases variable. Carbon acts in the great majority of its compounds as a quadrivalent element, but substances are known in which it is only bivalent. For instance, the compound carbonic oxide CO contains only one atom of bivalent oxygen, and one atom of carbon, which, therefore, must also be bivalent. What has become of the other two "valencies" of the carbon atom? It has been said that they "satisfy" each other, and the graphic formula has accordingly been written $<C=O$. But this explanation is meaningless, and, besides, does not apply to compounds like nitric oxide, NO, in which an atom with an even number of "valencies" (oxygen, dyad) is combined with an atom with an odd number (nitrogen, triad or pentad); for then, as the spare "valencies" can only satisfy each other in pairs, there is always one left over. A more justifiable mode of writing the formula of carbonic oxide is $:C=O$, where the two dots stand for blanks which can be filled up directly by two univalent atoms, for instance, by two atoms of chlorine to form phosgene (p. 91). Compounds like carbonic oxide which can directly take up univalent atoms into the molecule are called "unsaturated" compounds (see Chapter XX.).

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CHAPTER XIX

SUBSTITUTION AND DOUBLE DECOMPOSITION

WE have defined equivalent weights, or equivalents simply, as the quantities of different elements or radicals which can combine with the same quantity of a given substance. For example, on p. 189, there is given a table containing the quantities of various elements which combine with $35\frac{1}{2}$ parts by weight of chlorine. Now, if we look at all the compounds thus formed we see that they may be regarded as being derived from hydrogen chloride by the substitution of the various quantities of the elements tabulated for 1 part by weight of hydrogen. Precisely the same thing appears in the other tables: thus the oxides of Table IV. may be supposed to be derived from water by the substitution of other elements for hydrogen in the proportions given in the last column.

This notion of substitution has already been met with in Chapter XIII. It was stated on p. 126 that the chloride corresponding to an oxide had two atoms of chlorine instead of one of oxygen; and that the corresponding nitrate had, in place of each oxygen atom, two groups of the composition represented by the formula NO_3. Here we see that in order to get a chloride or a nitrate we have simply to replace the oxygen of an oxide by the equivalent amount of chlorine, or of the salt radical NO_3. In general, equivalents are capable of replacing, or being substituted for one another. It may

not be possible always to effect the actual substitution directly, but it is often convenient for many purposes to imagine that a whole series of substances may be derived from each other by the substitution of one atom or radical for another. We have looked at salts, for instance, as being formed from acids and bases by a part of the acid (the salt radical, Cl, NO_3, SO_4, etc.) taking the place of the oxygen of the oxide, or by the metal taking the place of the hydrogen of the acid. This brings the salts into the same series as the basic oxides on the one hand, and as the acids on the other.

A few examples of direct substitution have already been given. On p. 131 it was stated that iron dipped into a solution of copper sulphate became coated with copper, a portion of it equivalent to the copper deposited being at the same time dissolved. This action takes place according to the equation—

$$Fe + CuSO_4 = FeSO_4 + Cu.$$

Here the iron replaces the copper directly. Another case was that of the lead tree (p. 132), where zinc is directly substituted for lead. Zinc, again, when it is dissolved in dilute sulphuric acid affords another instance of direct substitution. The equation representing the action is—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

The zinc expels the hydrogen from its compound with the salt radical SO_4 by directly taking its place.

Comparable to this substitution of one metallic radical for another, we have cases where one salt radical takes the place of another. Thus chlorine when added to the solution of an iodide at once liberates iodine, a chloride being simultaneously formed, *e.g.*—

$$2KI + Cl_2 = 2KCl + I_2.$$

Many reactions which are usually spoken of as being

cases of direct substitution are really instances of double substitution, or mutual replacement. For example, if we expose marsh-gas or methane CH_4 to the action of chlorine in diffused daylight, the first action that occurs is the replacement of one atom of hydrogen by an atom of chlorine. When we consider the molecular equation which represents this reaction, we see that the replacement is not a simple one—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

Besides the substitution of one atom of chlorine for one atom of hydrogen in the methane molecule to form methyl chloride, there is the substitution of one atom of hydrogen for one atom of chlorine in the chlorine molecule to form hydrogen chloride. This at first sight apparently simple replacement is then in reality a mutual replacement, or **double decomposition** as it is sometimes called.

Instances of what might appear to be simple additions also turn out on investigation to be double decompositions—for example, the combination of hydrogen and chlorine to form hydrogen chloride. This takes place according to the equation—

$$H_2 + Cl_2 = 2HCl;$$

or, if we write down the molecular formulæ in full—

$$HH + ClCl = HCl + HCl.$$

Here we perceive that one atom of the hydrogen molecule is replaced by one atom of chlorine; but at the same time one atom of the chlorine molecule is replaced by one atom of hydrogen. Thus the reaction is a double decomposition and not a simple combination.

On considering a series of salts, such for instance as the sulphates, we find that they all agree in certain general properties and bear considerable resemblance to each other, so that it would appear that the substitution

of one metal for another does not altogether change the nature of a compound. This idea of the replacement of one element by another without the type of the compound changing was of great importance in the development of theoretical chemistry. Acetic acid is a compound having the formula $C_2H_4O_2$. We can substitute successively for three of the four atoms of hydrogen represented in the formula three atoms of chlorine, and still obtain substances which are of the same type as acetic acid. Notwithstanding the striking dissimilarity of the elements hydrogen and chlorine, these substitution products of acetic acid resemble the parent substance in their general chemical characters. The influence of the chlorine appears, however, when we study the strength of the acids produced. Acetic acid is itself a feeble acid, but as chlorine replaces the hydrogen in it atom for atom, the strength of the resulting acid always becomes greater. Trichloracetic acid is almost as powerful as the strong mineral acids, hydrochloric acid and nitric acid. The fourth atom of hydrogen in acetic acid cannot be replaced by an atom of chlorine; this serves as an indication that three hydrogen atoms in the molecule differ from the fourth. The subject will be referred to again in the next chapter.

In accordance with the recognition of the possibility of replacing one element by another without altering the general character of the compound in which the substitution took place, a theory of "types" was brought forward (1839) to account for the behaviour of chemical substances. Just as we might call acetic acid the parent type of the chloracetic acids, so the "types" chosen were supposed to be the parent substances from which all others were derived. The chief types were hydrogen $\left.\begin{matrix}H\\H\end{matrix}\right\}$, water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, and ammonia $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$; and along with them there existed secondary types such as hydrochloric

acid $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, sulphuretted hydrogen $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, phosphuretted hydrogen $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$. From these types other substances were derived by the substitution of various elements and radicals for the atoms of hydrogen contained in the types. For example, if we replace one atom of hydrogen in each by the radical CH_3, we obtain the compounds $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$ methane, $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$ methyl alcohol, $\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N$ methylamine, $\left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}$ methyl chloride, $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}S$ methyl mercaptane, $\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}P$ methyl phosphine. It was found, however, that these types were insufficient for the derivation of many substances by substitution, so "double," "multiple," and "mixed" types had to be introduced. Double and multiple types were simply one of the ordinary types written down more than once. Thus the double type of water is $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$, from which might be derived, for instance, sulphuric acid $SO_2\left\{\begin{matrix}H\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$ by the substitution of the bivalent radical SO_2 for two univalent hydrogen atoms. Mixed types were composed of two or more simple types of different kinds. Thus from the mixed type of hydrochloric acid and water $\left.\begin{matrix}Cl\\H\\H\\H\end{matrix}\right\}O$ there was derived chlorosulphonic acid $SO_2\left\{\begin{matrix}Cl\\H\end{matrix}\right\}O$ by the substitution of the radical SO_2 for two hydrogen atoms as before. It should be noted that the bivalent (or, in

general, the multivalent) radical or atom was supposed to replace hydrogen atoms belonging to *different* simple types, and thus, as it were, to bind the whole molecule together. It was from the consideration of compounds with such multiple and mixed types that the modern theories of valency and "atom-linking" (p. 195) originated.

A very important class of double decompositions is that taking place amongst acids, bases, and salts. When an acid neutralises a base (oxide or hydroxide), the hydrogen of the acid changes places with the metal of the base; and the oxygen or hydroxyl of the base with the salt radical of the acid; thus for example—

$$K(OH)+HCl=KCl+H(OH).$$

A reaction perfectly analogous to this is the expulsion of a weak acid from one of its salts in solution by a strong acid; for instance, the following equation represents the displacement of acetic acid from potassium acetate by hydrochloric acid—

$$K(C_2H_3O_2)+HCl=KCl+H(C_2H_3O_2).$$

If we compare the two foregoing equations we see that they are very similar, the radical $(C_2H_3O_2)$ in the second playing the part of hydroxyl (OH) in the first.

When solutions of two neutral salts are mixed the resulting solution is in general also neutral. From this fact J. B. Richter (not C. F. Wenzel, as is still often erroneously stated) drew the conclusion that if there were double decomposition between the salts, and the acid of the one formed a neutral salt with the base of the other, then the base of the first which was left must just suffice to neutralise the acid of the second; and further, from this, that the quantities of two acids which are sufficient to neutralise a given quantity of a base stand to each other in the same ratio, no matter what the base may be. These deductions, made at the end

of last century, were the beginnings of our knowledge of combining proportions. If two salts in solution are mixed, *does* double decomposition in general take place between them? Suppose we take solutions of potassium chloride and of sodium nitrate, and mix them, do these bodies still continue to exist in the solution, or do they enter into double decomposition with formation of sodium chloride and potassium nitrate according to the following equation—

$$KCl + NaNO_3 = NaCl + KNO_3.$$

It might be thought that information could be obtained by evaporating off the water and finding what solid salts crystallise out. This is not so, however, for it depends on the temperature at which the crystallisation takes place which of them comes out first. Any of the four may separate out according to circumstances; the one which is least soluble under the given conditions is the first to appear as a solid. The reaction then would seem to be a balanced one, quantities of all the salts being simultaneously present. This view is confirmed by the fact that we obtain the same solution whether we start from potassium chloride and sodium nitrate, or from potassium nitrate and sodium chloride. If one of the products is insoluble, then the balance is destroyed and the reaction proceeds the whole way. For example, potassium chloride and silver nitrate generate by their double decomposition silver chloride and potassium nitrate—

$$AgNO_3 + KCl = AgCl + KNO_3.$$

But silver chloride is insoluble in the solution and so falls out as a precipitate, being thus removed from the sphere of action. The interaction therefore goes on until all the silver, or all the chlorine in the solution, is precipitated (compare p. 157).

All these matters present a somewhat different aspect

when viewed in the light of the dissociation theory of salt solutions. We saw in Chapter XVII. that salts such as potassium nitrate, sodium chloride, potassium chloride, and sodium nitrate were supposed in their dilute solutions to be practically all resolved into ions; that the same held good for strong acids and strong bases, such as hydrochloric acid and potassium hydroxide; but that weak acids, such as acetic acid, were very little dissociated. In what follows we will assume, for simplicity's sake, that the salts and strong acids are entirely dissociated, while acetic acid is not appreciably dissociated at all into ions.

Let us now write the equations of this chapter according to the dissociation theory, indicating unit electrochemical charges by + and − attached to the symbols of the ions. For the neutralisation of potassium hydroxide by hydrochloric acid we have—

$$\overset{+}{K} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{K} + \overset{-}{Cl} + HOH.$$

But this equation contains useless terms, which appear on both sides of it. Striking these out we have left—

$$\overset{+}{H} + \overset{-}{OH} = HOH.$$

This shows that neutralisation in dilute solution consists merely in the formation of water from the ions hydroxyl and hydrogen, which cannot exist in presence of each other, but immediately unite to form water. The view here put forward is borne out by the fact that the heat evolution, the change of volume, and other phenomena attendant on the chemical action are the same in amount for the neutralisation of equivalent quantities of all strong bases by all strong acids. The effects being the same, it is highly probable that the reaction causing them is the same.

The expulsion of a weak acid from its salt by a strong acid (p. 203) now appears as follows—

$$\overset{+}{K}+\overset{-}{C_2H_3O_2}+\overset{+}{H}+\overset{-}{Cl}=\overset{+}{K}+\overset{-}{Cl}+HC_2H_3O_2.$$

Again striking out K and Cl from both sides, we obtain—

$$\overset{-}{C_2H_3O_2}+\overset{+}{H}=HC_2H_3O_2,$$

so that what really occurs is the formation of undissociated acetic acid from the ions hydrogen and "acetion."

We have next to look at what takes place on the mixture of salt solutions. Writing the equation given on p. 204 for the double decomposition of potassium chloride and sodium nitrate, we get—

$$\overset{+}{K}+\overset{-}{Cl}+\overset{+}{Na}+\overset{-}{NO_3}=\overset{+}{K}+\overset{-}{NO_3}+\overset{+}{Na}+\overset{-}{Cl}.$$

Now one side of this equation is precisely the same as the other, the order merely in which the ions are written down being different. No reaction, therefore, has taken place at all. This is extremely probable, because no heat is given out on the mixture of two dilute salt solutions such as the above, no change of volume occurs, and in fact there is no external sign of chemical reaction. In the case where silver nitrate is taken instead of sodium nitrate, a reaction does go on accompanied by evolution of heat, change of volume, etc., thus—

$$\overset{+}{K}+\overset{-}{Cl}+\overset{+}{Ag}+\overset{-}{NO_3}=\overset{+}{K}+\overset{-}{NO_3}+AgCl,$$

or

$$\overset{+}{Ag}+\overset{-}{Cl}=AgCl.$$

The silver ions unite with the chlorine ions to form silver chloride, which is precipitated.

On p. 199 we give as an example of substitution the

replacement of iodine by chlorine from a solution of potassium iodide. Written according to the dissociation theory the equation representing this is—

$$\overset{+}{K}+\overset{-}{I}+\overset{+}{K}+\overset{-}{I}+Cl_2=\overset{+}{K}+\overset{-}{Cl}+\overset{+}{K}+\overset{-}{Cl}+I_2,$$

or

$$\overset{-}{I}+\overset{-}{I}+Cl_2=\overset{-}{Cl}+\overset{-}{Cl}+I_2.$$

The free chlorine takes the electrical charges from the iodine ions and becomes chlorine ions, the iodine becoming at the same time ordinary free iodine. The potassium has nothing to do with the reaction except to keep enough positive electricity in the solution to balance the negative charges, which simply pass from the iodine atoms to the chlorine atoms.

CHAPTER XX

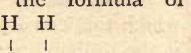
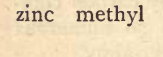
CHEMICAL CONSTITUTION

In the chapter on equivalence we learned that it is important for the chemist to know not only what and how many atoms enter into the composition of a molecule, but also how these atoms are arranged. On the theory of valency as developed in that chapter, the atoms in a complex molecule cannot all be united to one another, but must be linked together, atom to atom, so as to form a kind of chain. To find how the atoms are linked in this chain—to find which are directly united—is the problem of chemical constitution. The problem may be solved analytically by breaking the chain in various places, and ascertaining what atoms go to form each of the fragments; or it may be solved synthetically by joining up shorter chains, the arrangement of the atoms in which is known. The validity of both these methods depends on the assumption that the relative arrangement of atoms in a chain is not altered when the chain is broken, or when it unites with another chain. This assumption holds good in general, but as there are numerous cases where it fails, great care must be exercised in determining the constitution of a chemical compound, lest the reactions from which the constitution is ascertained involve internal rearrangements of the atoms amongst themselves. At best we can only say that a certain constitution for a given compound is

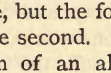
probable, but the greater the number of reactions from which this constitution has been ascertained the greater is the probability; and in the case of many carbon compounds the reactions studied have been so numerous that the probability amounts to practical certainty.

On p. 196 we attributed to zinc methyl the graphic or structural formula $H-\overset{H}{\underset{H}{C}}-Zn-\overset{H}{\underset{H}{C}}-H$, and we shall now look at the degree of probability which attaches to this formula as representing the manner in which the atoms are linked to each other. First of all, we know from the quantitative analysis of the compound, and from the determination of its vapour density, that its molecular formula is ZnC_2H_6. Now in all the compounds of hydrogen that have been obtained, hydrogen appears only as a univalent atom; carbon in the vast majority of its compounds must be assumed to be quadrivalent; and zinc in its chloride, the vapour density of which is known, is bivalent. Knowing then the number of atoms in the molecule of zinc methyl and the valency of these atoms, we may proceed to construct a probable constitutional formula for the compound from this information alone. It is evident, if the "valencies" are to "satisfy" each other, that the zinc atom and the two carbon atoms must form some sort of continuous chain, for hydrogen atoms being univalent, *i.e.* capable of uniting with only *one* atom, can take no part in linking together other atoms.

For the skeleton chain then, we have $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Zn-$, or $-\overset{|}{\underset{|}{C}}-Zn-\overset{|}{\underset{|}{C}}-$, the "valencies" being indicated by the short lines attached to the atomic symbols. In each formula there are six "unsatisfied valencies"; but there are exactly six univalent hydrogen atoms in the molecule

to fill up these blanks; so that the formula of zinc methyl may be written  , or  . In this way, from the mere consideration of the molecular formula and the general theory of valency, we have narrowed down the possible constitutional formulæ for zinc methyl to two. Without further information we cannot decide which of the two is the more probable, but the following reactions yield evidence in favour of the second. Zinc methyl may be formed by the interaction of an alloy of zinc and sodium, with methyl iodide, which can only have the structural formula . The equation representing the reaction is—

$$ZnNa_2 + 2CH_3I = ZnC_2H_6 + 2NaI.$$

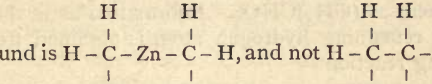
This would appear to be a double decomposition, the methyl groups  and the sodium atoms changing places; this lends probability to the view that the compound ZnC_2H_6 contains two methyl groups. Again, when bromine acts on the compound, zinc bromide and methyl bromide are formed according to the following equation—

$$ZnC_2H_6 + 2Br_2 = ZnBr_2 + 2CH_3Br.$$

This confirms the view stated above. When water acts on zinc methyl, zinc hydroxide and marsh-gas (methane) are produced—

$$ZnC_2H_6 + 2H_2O = 2CH_4 + Zn(OH)_2.$$

In all these reactions the two carbon atoms which are produced from the molecule of zinc methyl, or which go to form zinc methyl, are never united to each other, but belong to different molecules (of methyl bromide, methyl iodide, or of methane). The probability therefore is that these carbon atoms are not united in the molecule of zinc methyl, and that the structural formula for this



compound is $H-C(H)(H)-Zn-C(H)(H)-H$, and not $H-C(H)(H)-C(H)(H)-Zn-H$.

Another example of the determination of the atomic structure of a compound may be studied in the case of acetic acid. This substance has the molecular formula $C_2H_4O_2$, and thus contains two quadrivalent carbon atoms, two bivalent oxygen atoms, and four univalent hydrogen atoms. That it contains the group methyl $\cdot CH_3$ is probable from the fact that when its sodium salt $C_2H_3NaO_2$ is heated with caustic soda, methane CH_4 is evolved, while sodium carbonate remains behind—

$$C_2H_3NaO_2 + NaOH = Na_2CO_3 + CH_4.$$

The fact that it only forms salts in which one atom of hydrogen of the acid is replaced by a univalent atom of a metal is sufficient to show that one of the four atoms of hydrogen is different from the other three (p. 201). It is therefore probable that the molecule of acetic acid contains a methyl group, and a fourth hydrogen atom which does not belong to this methyl group. If we take methyl iodide, and treat it with potassium cyanide, we obtain potassium iodide and methyl cyanide by double decomposition—

$$(CH_3)I + K(CN) = (CH_3)(CN) + KI.^1$$

[1] The salts obtained in this and the previous reactions are produced by methods quite different from the modes of salt formation described in Chapter XIII.

Now this same methyl cyanide is formed along with water when ammonium acetate is heated with dehydrating agents, thus—

$$C_2H_3NH_4O_2 = (CH_3)(CN) + 2H_2O.$$

Here we have further proof of the existence of the methyl group in the acetic acid molecule. We may now with considerable confidence write the formula for acetic acid as $(CH_3)CHO_2$. Information as to the place of the remaining hydrogen atom is obtained from the following reaction—

$$(CH_3)CHO_2 + PCl_5 = (CH_3)COCl + POCl_3 + HCl.$$

Here the group OH is removed from the acetic acid molecule, and a chlorine atom is substituted for it, the compound so formed being called acetyl chloride. The formula is therefore probably $(CH_3)CO(OH)$. CH_3 and OH are both univalent groups, and therefore cannot be directly united (compare p. 209). They must be united to the group CO. But acetic acid behaves always as a "saturated" compound, that is, it never combines directly with univalent atoms or radicals (as carbonic oxide does, for example, p. 197); it therefore contains no unsatisfied valencies. The distribution of the valencies in the group CO must therefore be $= C =$ O, or CO must act as a bivalent radical, and to this the two univalent radicals

$$-\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H \text{ and } -O-H$$

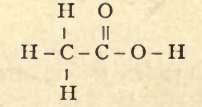
must be joined. We may therefore give as a probable graphic formula for acetic acid the scheme

$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O-H.$$

Just as molecular formulæ are obtained from the results of qualitative and quantitative analysis, and from

determinations of the vapour density, etc., and serve to put these results in a concise fashion before us, so a graphic formula such as we have given for acetic acid is deduced from a number of actions into which acetic acid enters as a reagent or as a product, and enables the experienced chemist to foresee a number of reactions into which acetic acid is probably capable of entering. The advantage of such structural formulæ is that they may be determined from a comparatively small number of well-chosen reactions, and, once they are determined, give a short expression for the general chemical behaviour of the substances they represent.

The graphic formula we have given to acetic acid was arrived at from the consideration of only a few reactions, and therefore to that extent has only a small degree of probability; but it is found that the other reactions of acetic acid agree very well with the formula, and so its probability is greatly enhanced. If we look at the formula



for a moment, we see it conveys a great deal of information in a very small space. First, if we count the number of bonds attached to the symbols of the various atoms, we find that the compound is saturated, for each carbon atom has four valencies "satisfied," each oxygen atom two, and each hydrogen atom one. We immediately see, too, that three atoms of hydrogen in the molecule will behave differently from the fourth, for three of them are attached to carbon, while the fourth is attached to oxygen. The three hydrogen atoms, too, which are united to carbon, should all behave alike, because they occupy precisely similar positions in the molecule, being all attached to the same atom of carbon. The two oxygen

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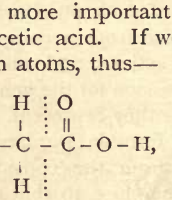
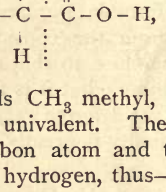
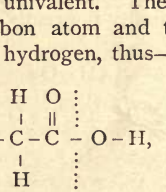
atoms in the molecule ought also to behave differently, for one of them is united to carbon alone, the other being united partly to carbon and partly to hydrogen. By splitting the chain at various places we obtain radicals. The break may be made between any two atoms, but the radicals produced in this way may be of very unequal general importance. The following diagrams exhibit the more important radicals which may be derived from acetic acid. If we make the split between the two carbon atoms, thus—



we obtain the radicals CH_3 methyl, and COOH carboxyl, which are both univalent. The split again may occur between the carbon atom and the oxygen atom which is also united to hydrogen, thus—



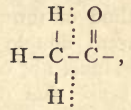
producing the univalent radicals CH_3CO acetyl, and OH hydroxyl. Another break is that between the same oxygen atom and the hydrogen atom—



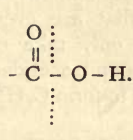
by which are produced an atom of hydrogen, H, and the radical acetoxyl CH_3·COO, the salt radical of the acetates. This break occurs to some extent when the

acid is dissolved in water, the fragments being charged with electricity, and thus becoming ions. The charged radical $CH_3 \cdot COO$ is called acetion (p. 206).

All these radicals are important, and enter into the composition of a great many compounds. They may be still further subdivided, giving rise to multivalent radicals. Thus acetyl may be split up as follows—



yielding univalent methyl and bivalent CO carbonyl. In the same way carboxyl becomes bivalent carbonyl and univalent hydroxyl—



The preceding examples will suffice to show the connection between the theory of radicals and the theory of valency as developed in the structural or graphic formulation of the molecules.

There is a large class of carbon compounds which are called *unsaturated* because they can unite directly with univalent elements such as hydrogen and the halogens. Such a compound, for instance, is ethylene C_2H_4, the structural formula for which is usually written $H_2C=CH_2$. In this formula two valencies of each of the carbon atoms are supposed to satisfy each other, although one from each is sufficient to hold the molecule together. The formula might therefore be written

H – C – C – H, the two unsatisfied valencies showing
    H   H
that the compound is capable of uniting with two univalent atoms or radicals. It should be mentioned that when two unsatisfied carbon atoms occur in a molecule they always occur as neighbours united to each other, so that the first method of formulation can always be adopted. The apparent double union of the carbon atoms in such formulæ must not be looked at as having any meaning in the sense that the two "bonds" hold the carbon atoms which they join, more firmly together than one "bond" would do. The reverse is the case. A carbon chain is more easily broken at a place where a "double bond" occurs than at a single bond. Compounds are known that are even less saturated than ethylene, which can only take up two atoms, say of bromine. The compound acetylene, C_2H_2, can take up four atoms of bromine to form $C_2H_2Br_4$. Its formula may be written $H-C\equiv C-H$, or

```
H – C – C – H.
    |   |
```

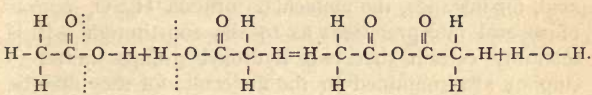
The first formula contains two carbon atoms united by "triple linking," which does not, however, hold them so closely combined as "single linking."

A simple example of the use of graphic formulæ to represent reactions may be taken in the formation of acetic anhydride (p. 136) from acetic acid. Acetic acid on being treated with certain dehydrating agents, loses water and becomes acetic anhydride. The molecular equation for the reaction is—

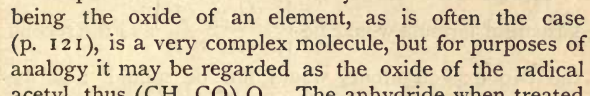
$$2C_2H_4O_2 = C_4H_6O_3 + H_2O,$$

but this does not show us in any way how the reaction actually proceeds. From the consideration of numerous interactions into which acetic anhydride enters, its

constitution and its graphic formula are well known, so that we may form a fairly clear conception of what takes place when the acid loses water to form the anhydride. The following equation exhibits the rearrangement of the atoms.



One of the acetic acid molecules splits into acetyl and hydroxyl: the other splits into hydrogen and acetoxyl. The hydrogen unites with the hydroxyl to form water, and the acetyl unites with the acetoxyl to form acetic anhydride. This then is really a case of double decomposition. The acid anhydride here instead of being the oxide of an element, as is often the case (p. 121), is a very complex molecule, but for purposes of analogy it may be regarded as the oxide of the radical acetyl, thus $(CH_3.CO)_2O$. The anhydride when treated with water is reconverted into acetic acid, the action being represented graphically as follows—



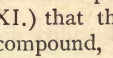
Here again we have a double decomposition, hydrogen changing places with acetyl, and hydroxyl with acetoxyl.

It is only in the case of the compounds of carbon that we possess anything like certain information regarding the molecular constitution. This arises from the fact that the number and diversity of the reactions into which the carbon compounds enter are so much greater than those of the compounds not containing carbon, and also that it is almost always easy to obtain a molecular formula for a carbon compound. Of course in the case of simple compounds of the other

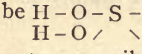
elements, such as H_2O or PCl_5, there can be no doubt as to the constitution—the univalent elements must be directly united to the multivalent element. But difficulty is at once experienced as soon as several multivalent atoms appear in the molecule. In the case of sulphuric acid, for instance, the molecular formula H_2SO_4 admits of several interpretations as to the constitution. It is tolerably certain that two hydroxyl groups united to sulphur are contained in the molecule, for they may be replaced by the action of phosphorus pentachloride (compare p. 212) by two atoms of chlorine. Thus the formula is $(HO)_2SO_2$, SO_2 being a bivalent radical. But what the constitution of this radical is we do not know. The sulphur atom in the sulphuric acid molecule may be tetrad or it may be hexad. In the first case the structural formula would be $\begin{matrix} H-O\diagdown & \diagup O \\ & S \\ H-O\diagup & \diagdown O \end{matrix}$: in the second the two oxygen atoms would not be united, and the formula would be $\begin{matrix} H-O\diagdown & \diagup\!\!=O \\ & S \\ H-O\diagup & \diagdown\!\!=O \end{matrix}$. The same uncertainty attaches to almost all the inorganic compounds: we can only make a guess at their probable structural formulæ.

There is a class of compounds, the so-called "molecular compounds," which we do not very well know how to treat on the theory of valency. They are practically all solid or liquid, and their molecular weights cannot be determined. According to the principles of valency discussed in Chapter XVIII. (p. 195), the conception is not directly applicable to such compounds at all. It is usual to write their formulæ as if they were made up of two or more molecules, thus we have $H_2SO_4,2H_2O$ to indicate a hydrate of sulphuric acid, and $MgCl_2,KCl,6H_2O$ to indicate a crystalline double chloride of magnesium and potassium containing water of crystallisation. How the atoms in such compounds are arranged

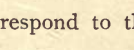
is quite uncertain. It is possible (although not probable, see Chapter XXI.) that the former compound may be a true atomic compound, that is a compound with an atom to atom linking in accordance with the ordinary rules of valency. Its formula should then be written H_6SO_6, and the only reasonable structural formula for it, on the assumption that sulphur in the molecule is hexad, would be



On p. 210 two possible graphic formulæ for zinc methyl were given. The reactions of the known substance correspond to the formula

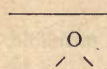


and we are not acquainted with any compound to which the formula



may be attributed. Still such a substance may be capable of existence, and we can confidently affirm that its properties will be quite different from those of zinc methyl. Yet there is no difference in the composition of the two bodies: it is only the arrangement of atoms in them that is not the same. There are many examples of such substances, which have the same composition, but possess a different constitution. They are termed *isomeric* substances, and in general have quite different properties from each other. For instance acetaldehyde differs entirely in its chemical behaviour from ethylene oxide, although both have the molecular formula C_2H_4O. The constitution of acetaldehyde is best expressed by the graphic formula

and that of ethylene oxide by the formula



A compound called diethylene dioxide is known, which has the same empirical formula as aldehyde and ethylene oxide, but double the molecular formula of these bodies, viz. $C_4H_8O_2$. Such a substance is said to be a *polymer* of the simpler substances.

CHAPTER XXI

THE PERIODIC LAW

We have learned in what has preceded that there are some sixty or seventy distinct chemical substances which have resisted all our attempts to decompose them into anything simpler. These simple substances have been named the *elements*, and it may not be unprofitable to look for a moment at the right they have to the name. Are our elements in truth undecomposable, or are they really compounds and are we merely unable to decompose them? It is impossible to give any definite answer to this question, and it may be left open without affecting our views on other chemical points at all. One thing we may be tolerably certain of, however, and this is, that if our well-known elements are really compounds, then they are all compounds of the same order, that order being different from that of the compounds of the elements amongst themselves. The reason for this statement is not far to seek. In Chapter XI. it was shown that the product of the atomic weight and specific heat of solid elements is nearly constant, and equal to 6·4 if the ordinary units for atomic weight and specific heat are adopted. We may express this relation in the form of a curve such as we used in Chapter XVI. On the horizontal axis (Fig. 3) we mark off the atomic weights of the elements, and erect perpendiculars at the points thus obtained to represent

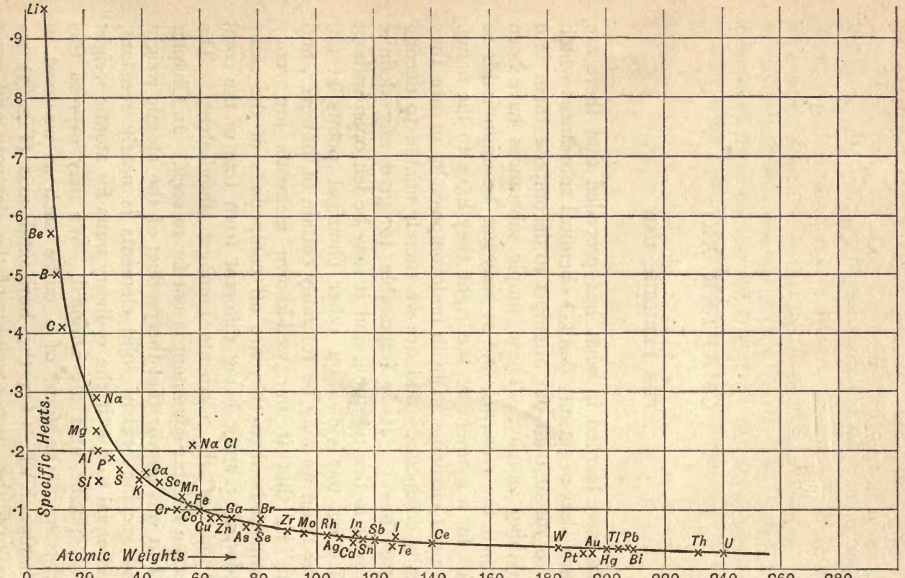

Specific Heats.
Atomic Weights
Li
Be
B
C
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Mn
Fe
Ni
Cr
Co
Cu
Zn
Ga
As
Se
Br
Zr
Mo
Rh
Ag
Cd
In
Sn
Sb
Te
I
Ce
W
Pt
Au
Hg
Tl
Pb
Bi
Th
U
·9
8
·7
·6
·5
·4
·3
·2
·1
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280

FIG. 3.

the specific heats in the solid state (p. 100) on the scale given by the vertical axis. By joining the tops of the perpendiculars, marked by small crosses in the figure, a somewhat broken and irregular curve would be obtained. If the product were quite constant and exactly equal to 6·4 instead of being only nearly so, the curve would be a smooth and regular one: this "theoretical" curve is indicated in the figure. Now all our solid elements obey Dulong and Petit's law, *i.e.* the product of their atomic weight and their specific heat is nearly constant; or when we make the construction of Fig. 3, the point obtained lies on the theoretical curve or close to it. This does not hold of compounds. Suppose for instance that sodium chloride was a substance which could not in any way known to us be decomposed, or built up from something simpler. For all we could learn directly it might then be an element. But a consideration of its specific heat would at least lend great probability to the assumption of its being a compound; for the product of the apparent atomic weight (the actual formula weight) and the specific heat would be not 6·4 but 12·5, and in the figure the point would fall quite away from the curve of specific heats. This point is indicated at the atomic weight $58·5 = 35·5 + 23$. We thus see that a distinction is at once drawn between elements and compounds as we know them, so that they must really be different classes of bodies altogether.

The same conclusion is reached when we tabulate properties of the elements other than the specific heat. Let us take for example the *atomic volume* after Lothar Meyer. Just as the atomic heat is the product of the atomic weight and the specific heat, so the atomic volume is the product of the atomic weight and the specific volume. The specific volume of a substance is the volume occupied by unit mass of that substance, and a little consideration will show that it is inversely proportional to the density. The process of tabulation is

precisely that adopted for the specific heat — atomic weights are measured on the horizontal axis, and atomic volumes perpendicular to this on the scale of the vertical axis. The points thus obtained do not lie, as with the specific heat, approximately on a continuous curve, but, as the lines in Fig. 4 indicate, on a series of somewhat irregular curves which resemble each other closely in general appearance. If the whole series is looked upon as a single curve, that curve is what is termed a *periodic* curve, *i.e.* one which after a certain interval repeats itself. Each repetition is called a period, and the periods have been marked in the figure by Roman numerals. It is only the elements which fall naturally into their place on this curve: compounds, if we take their formula weight as representing the atomic weight, fall far away from it, so that we are again justified in assuming that our elements are not compounds in the ordinary sense, which we have simply been unable to decompose.

The periodic character of this curve shows the existence of many relations which do not appear in the curve of specific heats. There are evidently two sorts of periods in the figure, the first two being very much smaller than the others. These are called the *short periods*: the others are *long periods*. We see at once from the curve that elements which occupy similar positions in the separate periods are similar in their chemical character. Thus the first element in each complete period, short or long, is an alkali metal, the second is a metal of the alkaline earths, and the last element a halogen. In general we may state that the elements on steep portions of the curve have very pronounced chemical characters, those on descending portions of the curve are base-forming, those on ascending portions are acid-forming. Elements at or near the minima cannot be said to be decidedly acid-forming or decidedly base-forming: in different stages of oxidation they may be either.

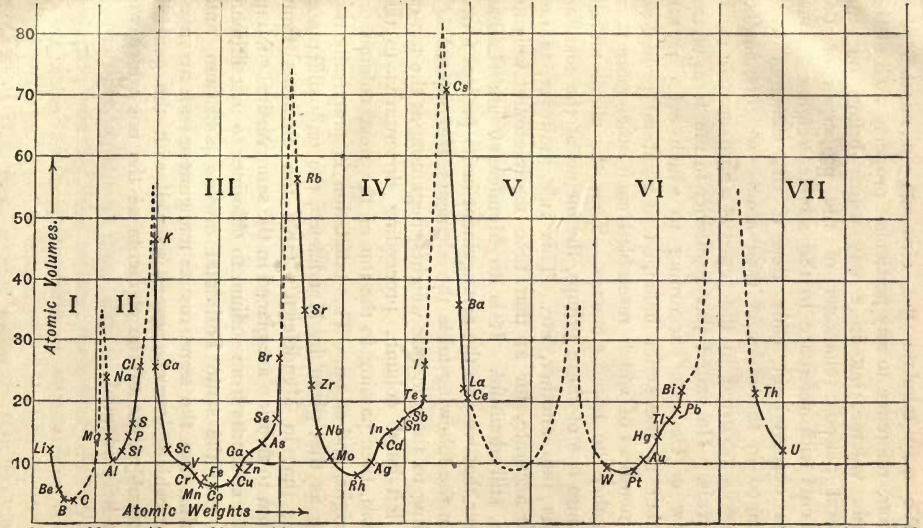

Atomic Volumes.
Atomic Weights
I
II
III
IV
V
VI
VII
Li
Be
B
C
Mg
Na
Al
Cl
Si
P
S
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Cu
Zn
Ga
As
Se
Br
Rb
Sr
Zr
Nb
Mo
Rh
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
W
Pt
Au
Hg
Tl
Pb
Bi
Th
U
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
10
30
50
70

FIG. 4.

We may tabulate the elements in another way without reference to any particular property such as the atomic volume, but in a way which brings out the general periodic character of the properties of the elements with reference to the atomic weights. Newlands observed in 1864 that if the elements were arranged in the order of their atomic weights, similar elements occurred in the series at approximately equal intervals. He stated this regularity in the form of the "Law of Octaves," according to which every eighth element in the series belonged to a natural group, all the members of which resembled each other more than they did the other elements. Thus the alkali metals fell into one of these groups, the metals of the alkaline earths into another, etc. This rule, however, is not quite accurate, for at that time many atomic weights were still doubtful. It is to Mendelejeff and Lothar Meyer that we owe the arrangement in its present form.

In the following table the elements are ordered according to their atomic weights, beginning at the top of the left-hand column, proceeding downwards to the bottom, then passing to the top of the next column on the right, and so on. This tabulation is practically the same as that given by Mendelejeff, the only difference being that in Mendelejeff's table the elements from lithium to fluorine are placed in the same vertical column as the elements from sodium to chlorine, so that lithium falls into the same horizontal row as potassium, and fluorine into the same row as manganese—an arrangement which scarcely agrees so well with the general chemical nature of the elements as the one which we have here adopted.

TABLE I.

			III.	IV.	V.	VI.	VII.	
1			K	Rb	Cs	—	—	Even Series
2			Ca	Sr	Ba	—	—	
3			Sc	Yt	La	Yb	—	
4			Ti	Zr	Ce	—	Th	
5			V	Nb	Di(?)	Ta	—	
6			Cr	Mo	—	W	U	
7			Mn	—	—	—		
8			Fe	Ru	—	Os		Transition Elements.
			Co	Rh	—	Ir		
			Ni	Pd	—	Pt		
1	Li	Na	Cu	Ag	—	Au		Odd Series.
2	Be	Mg	Zn	Cd	—	Hg		
3	B	Al	Ga	In	—	Tl		
4	C	Si	Ge	Sn	—	Pb		
5	N	P	As	Sb	—	Bi		
6	O	S	Se	Te	—	—		
7	F	Cl	Br	I	—	—		
	I.	II.	III.	IV.	V.	VI.	VII.	

The vertical columns represent periods, which are denoted by the same Roman numerals as in Fig. 4. Here again we see the two short periods and the five long periods. A complete short period contains seven elements—a complete long period seventeen, which are made up of two series of seven elements each, and a transition group of three elements. Within any one period, whether short or long, there is no sudden change in general chemical properties as we pass from one element to the next in order. Descending any series we proceed from base-forming elements, through elements whose oxides are neither strongly acid nor strongly basic,

to acid-forming elements. In the short periods, which consist of only one series, we start from elements which form powerful bases and end with elements which form powerful acids. In the long periods, the uppermost or *even* [1] series start with strong base-forming elements, but end with metals forming both acid and basic oxides; the *odd* series, on the other hand, begin with only moderately strong base-forming elements and end with elements which are very markedly acid-forming. The elements connecting the odd and even series in the long periods are intermediate in their behaviour between the elements they connect; those of the first row (iron, ruthenium, osmium) forming acids as well as bases, the others forming only bases.

When we pass from one period to the next, there is a sudden change in the properties of the elements with consecutive atomic weights. Thus the last element of Period I., F = 19, is in complete contrast in its chemical nature to the next element, Na = 23, which belongs to Period II. The same thing happens in the case of the long periods; iodine, the last member of Period IV., forms powerful acids; whilst cæsium, the first member of Period V., is the most powerful base-forming element we know. These sudden changes in the chemical properties correspond in Fig. 4 to sudden changes in the direction of the curve; between fluorine and sodium, and again between iodine and cæsium, the curve, from being an ascending curve, changes into a descending curve.

If we consider the elements in a horizontal row, denoted by an Arabic numeral in the table, we find that they are on the whole such as would naturally fall together in a classification of the elements according to their general chemical characters. Thus in the first row we have potassium, rubidium, and cæsium, metals of the strong alkalies; in the second row calcium, stron-

[1] The terms *odd* and *even* refer to the numbers given to the series in the original periodic table of Mendelejeff.

tium, and barium, metals of the alkaline earths; and so on. It will be observed that the numbers of the rows in the table are repeated, running in order from 1 to 8, and then beginning again at 1. There are therefore two rows, one in the even and one in the odd series, which are represented by the same number. Between the members of these two rows there is a general similarity of properties, although it is not so great as that between members of the same row. Thus the compounds of vanadium, niobium, etc., in the even series bear considerable resemblance to those of phosphorus, arsenic, bismuth, etc. in the odd series. The most striking property which exemplifies this is the combining capacity or valency of the elements. All the elements of two rows indicated by the same number, form, in general, compounds with precisely similar formulæ. Take, for example, the "highest" oxides, *i.e.* the oxides containing most oxygen, of the rows marked 5, which form the two subdivisions of one natural group. We find their formulæ to be—

Group 5	Even series			V_2O_5	Nb_2O_5	—	Ta_2O_5
	Odd series	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	—	Bi_2O_5

Two atoms of all the elements of Group 5, then, combine with five atoms of oxygen. The same thing holds good for other groups, only the combining capacity is different from that of Group 5. It increases regularly from Group 1 to Group 8, as may be seen in Table II., where, instead of the elements of Table I. we have tabulated the oxides of these elements. In the case of elements forming more than one oxide, the highest salt-forming or acid-forming oxide is taken in almost all cases. The oxides enclosed in brackets are not known, but are the anhydrides of well characterised series of salts.

TABLE II.

Group.		III.	IV.	V.	VI.	VII.	
1		K_2O	Rb_2O	Cs_2O	—	—	Even Series.
2		Ca_2O_2	Sr_2O_2	Ba_2O_2	—	—	
3		Sc_2O_3	Yt_2O_3	La_2O_3	Yb_2O_3	—	
4		Ti_2O_4	Zr_2O_4	Ce_2O_4	—	Th_2O_4	
5		V_2O_5	Nb_2O_5	?	Ta_2O_5	—	
6		Cr_2O_6	Mo_2O_6	—	W_2O_6	U_2O_6	
7		Mn_2O_7	—	—	—		
8		Fe_2O_6)	Ru_2O_8	—	Os_2O_8		Transition Elements.
		Co_2O_3	Rh_2O_4	—	Ir_2O_4		
		Ni_2O_3	Pd_2O_4	—	Pt_2O_4		
1	Li_2O	Na_2O	Ag_2O	—	Au_2O		
2	Be_2O_2	Mg_2O_2	Zn_2O_2	Cd_2O_2	—	Hg_2O_2	Odd Series.
3	B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	—	Tl_2O_3	
4	C_2O_4	Si_2O_4	Ge_2O_4	Sn_2O_4	—	Pb_2O_4	
5	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	—	Bi_2O_5	
6	—	S_2O_6	(Se_2O_6)	Te_2O_6	—	—	
7	—	(Cl_2O_7)	—	I_2O_7	—	—	
	I.	II.	III.	IV.	V.	VI.	VII.

In order that the amounts of oxygen in the various oxides may be readily compared, the formulæ have been

written throughout so as to contain two atoms of the element combined with oxygen. We have consequently written, for example, C_2O_4 for carbonic anhydride instead of the proper molecular formula CO_2. The number of the group will be seen, with few exceptions, to correspond to the number of oxygen atoms which combine with two atoms of the various members of the group.

The same sort of regularity appears when we tabulate the highest chlorides, bromides, etc., instead of the oxides; but in these cases there are more exceptions. The highest chlorides of the elements of the even series may be given as examples.

TABLE III.

	III.	IV.	V.	VI.	VII.
1	KCl	$RbCl$	$CsCl$	—	—
2	$CaCl_2$	$SrCl_2$	$BaCl_2$	—	—
3	$ScCl_3$	$YtCl_3$	$LaCl_3$	$YbCl_3$	—
4	$TiCl_4$	$ZrCl_4$	$[CeCl_3]$	—	$ThCl_4$
5	$[VCl_4]$	$NbCl_5$	—	$TaCl_5$	—
6	$[CrCl_3]$	$[MoCl_5]$	—	WCl_6	$[UCl_4]$
7	$[MnCl_4?]$	—	—	—	—

We here perceive that there is a general correspondence between the group number and the number of chlorine atoms with which one atom of the elements can combine, but that there is a tendency of the elements in the higher groups to combine with fewer atoms than are given by the group number. The exceptions to the strict rule have been enclosed in brackets.

When we study the compounds of the elements with hydrogen or the alcohol radicals (Chapters XVIII. and XX.), we find that the combining capacity of the different groups varies somewhat differently from before. In the first place it is almost exclusively elements of the odd series which can combine with hydrogen or the alcohol radicals to form definite compounds. As we

proceed downwards in any odd series, we find that the combining capacity does not now steadily increase, but reaches a maximum at Group 4, after which it decreases regularly.

Thus in the first period we have—

Group.	Methyl Compounds.	Hydrogen Compounds.
1	$Li(CH_3)_1$	—
2	$Be(CH_3)_2$	—
3	$B(CH_3)_3$	BH_3
4	$C(CH_3)_4$	CH_4
5	$N(CH_3)_3$	NH_3
6	$O(CH_3)_2$	OH_2
7	$F(CH_3)_1$	FH

The power of combining with hydroxyl groups seems to be determined by the number of hydrogen atoms with which the element can unite. This may be seen in the following table, which gives the compounds of the elements in the second period which contain most hydroxyl groups—

Group.	Compounds.	Formulæ.
1	Sodium hydroxide	$Na(OH)_1$
2	Magnesium hydroxide	$Mg(OH)_2$
3	Aluminium hydroxide	$Al(OH)_3$
4	Silicic acid	$Si(OH)_4$
5	Phosphoric acid	$PO(OH)_3$
6	Sulphuric acid	$SO_2(OH)_2$
7	Perchloric acid	$ClO_3(OH)_1$

Corresponding to the oxide P_2O_5 there should be the hydroxide $P(OH)_5$, if for all the oxygen the equivalent amount of hydroxyl were introduced. But this compound, $P(OH)_5$, does not exist, the acid $PO(OH)_3$, orthophosphoric acid, being the compound with the greatest number of hydroxyl groups in the molecule, in accordance with the fact that there is a hydrogen compound PH_3, but no hydrogen compound PH_5.

It has been pointed out that not only elements in the same horizontal row are similar, but that the properties

of the consecutive elements in the vertical series do not change suddenly. We should therefore expect to find a general resemblance amongst the elements gathered together in one part of the table. Such a general resemblance does in fact appear. The upper rectangle formed by the dotted lines in Table I. contains the rare metals of the earths which occur in groups in a few minerals found only in certain localities, and which from their similarity of chemical properties are extremely difficult to separate from one another. The lower rectangle contains all the "metallurgical" elements, *i.e.* the heavy metals which are prepared on the large scale from their ores. The elements enclosed in this rectangle are, however, not all of technical importance. Bordering on these elements are the light metals, sodium, magnesium, and aluminium; and the half-metals, arsenic, antimony, and bismuth,—all of which are met with in commerce.

When we look at the position of the elements composing these groups on the curve of Fig. 4, we find that the metals of the rare earths occupy the middle of the descending portions of the curve in the long periods, and that the "metallurgical" metals lie at or immediately after the minima.

It is difficult to distinguish sharply between metals and non-metals, for the properties of the one class merge gradually into those of the other (compare Chapter II.). However there exists a classification which is generally adopted in practice (p. 14), and this classification is in conformity with the periodic table. The elements enclosed in the dotted triangle in the lower left-hand corner of Table I. are the non-metals as usually understood. All the other elements are metals.

It will be observed that hydrogen occupies no place in the foregoing tables and curves. Having the lowest atomic weight it occupies of course the first position amongst the elements, but between it and the element

with the next greatest atomic weight (Li = 7) there exists a gap in the table. Hydrogen and lithium are both univalent elements, so that they might be expected to belong to the same group, and hydrogen further resembles lithium and the other univalent metals in its compounds with the salt radicals, in which it plays the part of a metal. It is therefore very probably the first representative of a short period, all the other members of which are missing.

As to the other blanks found in Table I., we may reasonably expect that some of them at least will be filled up by elements hitherto undiscovered, and that the new elements will be of the same kind as those we already know. When the table was first constructed, the number of blanks in it was greater than now, and Mendelejeff was bold enough to predict the existence of elements to fill the gaps. His predictions have been more than once fulfilled. The three well-defined elements—gallium, germanium, and scandium have all been discovered since his formulation of the periodic law, and have fallen naturally into their places in the third period. Mendelejeff not only predicted the existence of these elements, but also their chief chemical and physical properties from a consideration of the properties of their nearest neighbours in the table. Subsequent experiment on the new elements entirely justified these predictions.

Another use to which the periodic table has been put is the correction of erroneous atomic weights. For instance, the atomic weight of tellurium was supposed to be greater than that of iodine, which caused iodine to come before tellurium in the periodic classification, so that it fell into the sulphur group, while tellurium fell into the halogen group. But this contradicts the whole chemical behaviour of these elements; for iodine from its properties must be classed along with chlorine and bromine, and tellurium naturally belongs to the sulphur

and selenium group. It was clear then that one or other of the atomic weights had been incorrectly determined. Fresh investigations were made, with the result that the atomic weight of tellurium was found to be considerably lower than the value formerly accepted, and below that of iodine. The atomic weights of some of the metals of Group 8 have also been revised for the same reason, and are now in accordance with the periodic law.

Most well defined properties of the elements are periodic, *e.g.* melting-point and magnetic power. When the numerical values are tabulated against the atomic weights, the curve obtained is broken up into similar periods like the curve of atomic volumes (Fig. 4), although the shape of the different periods depends upon the property examined. The regular non-periodic curve obtained for the specific heat (Fig. 3) is quite exceptional. Not only are the properties of the elements themselves periodic, but the properties of their corresponding compounds are also periodic. Thus if we tabulate the heat given out on the formation of the chlorides from their elements against the atomic weights of the elements which combine with the chlorine, a periodic curve results. The same periodicity is observed in the molecular volumes (= molecular weight × specific volume) of the oxides, and in the melting and boiling points of various corresponding compounds.

The classification of the elements afforded by the periodic table, although most valuable, is not in every respect quite satisfactory. We find, for example, lithium and sodium in the same group as copper, silver, and gold, to which metals they undoubtedly bear considerable resemblance in their forms of combination, but their real place is with potassium, rubidium, and cæsium. The curve of atomic volumes shows this satisfactorily. Again, elements which resemble each other so much as copper and mercury do, are found in different

groups in the periodic classification. The three first members of the first period show in their general chemical behaviour many similarities, not only to their neighbours in the same group, but to their neighbours in the next group. Thus lithium in many respects resembles magnesium; the bivalent metal beryllium bears such a strong similarity to the trivalent metal aluminium, that it was itself long thought to be trivalent; and boron resembles no other element so much as silicon. These irregularities, however, do not impair the great theoretical significance of the periodic classification, although for practical purposes the elements have often to be subjected to a different arrangement.

INDEX

ABSOLUTE zero, 76
Absorption-coefficient, 162
Absorption of gases by solids, 23, 38, 172
—— —— heat in chemical change, 29, 35
Acid reaction, 123
—— salts, 129
Acids, 122
—— basicity of, 128
Acidity of bases, 128
Action, chemical, 16
—— —— balanced, 148
—— —— characteristics, 26
—— —— conditions, 16
—— nascent, 69
—— of mass, 153
Active mass in gases and solutions, 153
—— —— of solids, 156
Affinity, 16
Aggregation, states of, 5
Alkaline reaction, 123
Allotropic modifications, 102
Amorphous solids, 10
Analysis, 12
Anhydrides, 122, 134
Anomalous vapour density, 153
Arrhenius, 184
Atom, 43
—— linking, 196, 203
Atomic heat, 101
—— volume, 223
—— weights, 44, 94, 190, 234
—— —— table of, ii.
—— —— unit of, 95, 105
Atomicity, 192
Avogadro's law, 88, 95, 142, 153
—— —— for solutions, 174

BALANCED action, 148-159
Bases, 122
Basic salts, 130
Basicity of acids, 128
Berthollet, A., 46
—— C. L., 40
Black, 9, 27
Boiling-point, 144
—— —— of solutions, 175
Bonds, 196, 203
—— double, 216
Boyle, 13, 50, 72
Boyle's law, 72, 87, 140
—— —— deviations from, 79
—— —— for solutions, 174
Bunsen, 162

CALX, 57
Catalytic action, 23
Cell, galvanic, 177
Celsius or Centigrade scale, 3
Change, chemical and physical, 7
Charles's law, 75, 87, 142
—— —— for solutions, 174
Chemical action, 7, 16, 26, 36
—— —— of electricity, 22, 177
—— —— of light, 21
—— —— of temperature, 17, 148
—— affinity, 16
—— combination, 16, 19, 25, 39
—— equations, 117
—— equilibrium, 148
—— formulæ, 109
—— symbols, 107
Clausius, 140, 183
Coefficient of absorption, 162
Combination, 16, 19, 25, 39
Combining capacity, 192, 229-232
—— proportions, constant, 39
—— —— multiple, 41
—— —— by volume, 46, 48
Combustibles, compound, 52
Combustion, 27, 50
—— nature of, 57

Compound radical, 127
Compounds, 12, 28
Concentration, 153, 173
Condensation of gases and vapours, 8, 143, 145
Conduction of electricity, 180
Conservation of energy, 31
—— of matter, 26
Constant proportions, 39
Constitution, 208
Contact, 16
—— action, 24
Critical temperature, 8
Crystals, 10

DALTON, 39-45, 88, 163, 190
Dalton's law of multiple proportions, 41
—— —— of partial pressures, 163, 170
Decomposition, 11, 16, 25
—— double, 200
Density, 81
—— maximum, of water, 82
—— of gases, 82, 93
—— of vapours, 86
—— relative, 82
—— standards of, 82, 83
Depression of freezing-point, 175
Deviations from Boyle's law, 79
Deville, 157
Diffusion of gases, 142
—— in solutions, 171
Displacement of acids, 203
Dissociation, 148
—— electrolytic, 184, 205
Double decomposition, 200
—— linking, 216
—— salts, 133
Dulong and Petit's law, 100, 223

ELECTRICITY, chemical action of, 22, 32
—— conduction of, 180
—— produced by chemical action, 29, 176
Electrochemical equivalence, 179, 187
Electrolysis, 176
Electrolytic dissociation, 184, 205
Elements, 12, 221
—— list, 13
—— periodic arrangement, 227
Elevation of boiling-point, 175
Endothermic reactions, 29
Energy, 30
—— conservation of, 31
Equations, 116
Equilibrium, 143
—— chemical, 148
—— mobile, 147
Equivalence, 187
Equivalents, chemical, 188
—— electrochemical, 179, 187
Exothermic reactions, 29
Expansion of gases, 75
Explosive combination, 17, 24, 32
—— decomposition, 35

FAHRENHEIT scale, 3
Faraday's law, 180, 194
Fixed proportions, 39
Formulæ, 109
—— constitutional, 196
—— empirical, 112
—— graphic, 196, 209
—— molecular, 111, 112
Formula-weight, 114
Freezing-point of solutions, 175

GALVANIC cell, 177
Gaseous molecules, 89
—— state, 5
—— volumes, 46
Gases, density, 82, 93
—— expansion by heat, 75
—— kinetic theory, 140
Gay-Lussac, 39, 46-48
Gram molecule, 110
—— —— volume, 111

HEAT, 4
—— atomic, 101
—— latent, 9
—— specific, 4, 100
Heat-effect, 28
Henry's law, 163, 170
Hoff, van 't, 172
Humboldt, 46

INSTABILITY, 36
Ions, 180, 205
Isomerism, 219
Isomorphism, 104

KINETIC energy, 30
—— equilibrium, 147
—— theory, 139

LATENT heat, 9
Lavoisier, 27, 58
Law, Avogadro's, 88, 95, 142, 153
—— Boyle's, 72, 141, 174
—— Charles's, 75, 142, 174
—— Dalton's (of partial pressures), 163, 170
—— Dulong and Petit's, 100, 223
—— Faraday's 180, 194
—— Henry's, 163, 170
—— of constant proportions, 39

Law of gaseous volumes, 46
—— of multiple proportions, 41
—— of octaves, 226
—— periodic, 221
Light, chemical action of, 21
Liquid state, 5
—— and vapour, 8, 143

Mass, 2
Mass-action, 153
Matter, conservation of, 26
Maxwell, 140
Measurement, 1
Mechanical separation, 37
Membranes, semipermeable, 173
Mendelejeff, 226, 234
Metals, 13, 233
Metric system, 1
Meyer, Lothar, 223, 226
—— Victor, 86
Mixtures, 15, 36, 45
Mobile equilibrium, 147
Molecular compounds, 218
—— volume, 235
—— weights, 92, 95
—— —— in solution, 175
—— —— unit of, 99
Molecules, 45
—— gaseous, 89, 140
Multiple proportions, 41

Nascent state, 69
Neutralisation, 203, 205
Neutrality, 125
Newlands, 226
Non-metals, 13, 233
—— —— list, 14
Normal pressure and temperature, 82

Octaves, law of, 226
Osmotic pressure, 172
Oxidation, 60, 62, 63, 70
Oxides, 60
—— classes of, 121
—— table of, 230
Oxidising agents, 66, 68

Partial pressure, 161
Periodic curve, 225
—— law, 221
—— table of elements, 227
Polymerism, 220
Pressure, 73
—— dissociation, 157
—— effect on chemical action, 22
—— —— on dissociation, 152
—— osmotic, 172
—— partial, 161
Pressure, standard, 82
—— vapour, 144
Priestley, 58
Proportions, constant, 39
—— multiple, 41
Proust, 40

Qualitative composition, 39, 41, 112
Quantitative composition, 39, 41, 112

Radical, compound, 126, 214
—— of salts, 126
Reducing agents, 66, 68
Reduction, 60, 66
Replacement, 198
Respiration, 58
Richter, J. B., 203
Rusting of iron, 65

Salt-formation, 124, 131, 210, 211
Salt-radical, 126
Salts, 121
—— acid, 129
—— basic, 130
—— double, 133
—— neutral, 125
—— normal, 129
—— table of, 136
Saturation, 166
Scales of temperature, 3
Semipermeable membranes, 173
Series of elements, 227
Shock, chemical effect, 22
Solids, 5
—— amorphous and crystalline, 9
Solubility, 162, 168
Solutions, 37, 160-175
—— electrolytic, 178, 181
—— saturated, 166
—— supersaturated, 167
Specific gravity, 82
—— heat, 4, 100
Stability, 32, 36
Standard pressure and temperature, 82
State, nascent, 69
—— of aggregation, 5
Structural formulæ, 196, 209
Substitution, 198
Supersaturation, 167
Supporters of combustion, 58
Symbols, 107
Synthesis, 12

Temperature, 3
—— absolutue zero of, 76
—— critical, 7

Temperature, effect on chemical change, 17
—— of dissociation, 149
—— of gases, 141
—— scales of, 3
—— standard, 82
Theory, atomic, 43, 190
—— kinetic, 139
—— of types, 201
Thermal capacity, 4
Thio compounds, 134
Triple linking, 216

UNITS, 1
—— of atomic weights, 95, 105
—— of density, 82, 83
—— of pressure, 73
Unsaturated compounds, 197, 215
Unstable compounds, 36

VALENCY, 192, 229
Van 't Hoff, 172
Vaporisation, 143
Vapour, 5
—— density, 86
—— —— anomalous, 153
—— pressure, 144
Volatilisation of solids, 8, 146
Volumes, atomic, 223
—— gaseous, 46
—— molecular, 235

WEIGHT and mass, 2
Weights, atomic, 44, 94, 234
—— molecular, 92, 95
—— —— in solution, 175
—— —— unit of, 99
Wenzel, 203
Work, 31
Wurtz, 154

ZERO, absolute, 76

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